Gasification of Victorian Brown Coal

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Agglomeration modelling, gasification reactivity, and broad assessment of catalysts for fuel gas cleaning and water gas shift reaction

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Summary

This project, funded by the Brown Coal Innovation Australia (BCIA) looked at the following aspects:

- Thermodynamic modelling to predict agglomeration behaviour of Victorian brown coal during gasification – in particular under temperature range relevant to fluidized bed conditions
- Preparation and testing of a number of catalysts for volatile cracking, gas cleaning and water gas shift reaction and carbon conversion. These catalysts include power station flyash, and Nickel Oxide and Iron Oxide supported on Char, Al_2O_3 and SiO_2.

In addition to the above, the work also included a comparison of gasification reactivity of four Victorian brown coals and a Rhenish lignite obtained from RWE of Germany. This was carried out in thermo-gravimetric analyser under CO_2 and steam gasification atmospheres.

The results of the thermodynamic modelling are presented in a companion report.

The thermodynamic modelling suggests that agglomeration is unlikely to take place during fluidized bed gasification of Loy Yang coal. However, agglomeration could be problem during fluidized bed gasification of Morwell and Yallourn coals. These predictions are broadly in line with our observations during High Temperature Winkler (HTW) gasification of these coals under the program run by the CRC for Clean Power from Lignite. If fluidized bed gasification continues to be explored for processing of brown coal, we recommend focussed and laboratory-based longer duration testing of Morwell and Yallourn coals to assess the mechanism of agglomeration during fluidized bed gasification.

The thermodynamic model developed for prediction of agglomeration behaviour will be useful for potential use in future when assessing gasification behaviour of Victorian brown coals.

All catalysts were found to be effective in volatile cracking, *ie*. generation of tar-free gas. However, we do not believe that catalysts are required for volatile cracking during gasification.

The major effect of catalysts is found to be on water gas shift reaction. We observed that flyash (collected from Yallourn power station) is not effective at all for water gas shift reaction, presumably because of their higher levels of crystallinity having been exposed to high temperature inside the boiler. On the other hand, Nickel Oxide and Iron Oxide supported on Char, Al_2O_3 and SiO_2 are effective for water gas shift reaction. However, we observed that chars on Char-supported catalysts disintegrate during the water gas shift reaction where steam is present as a reactant. This raises question about the viability of the use of char-supported catalysts continuously in water-gas shift reactors, in particular char from Victorian brown coal which are known to be soft and friable. Considerable effort and trials have to be made to generate char as a support for catalysts, if char from Victorian brown coal is considered for use as a support base for Nickel or iron catalysts.

In addition, Nickel oxide powder is known to be toxic, and therefore its use over a longer-term as a shift catalyst will come under increasing scrutiny. We recommend more focussed work on Fe-based catalysts, supported on either Alumina or Silica base. The work should concentrate on improving and sustaining the activity of such catalysts.

A clear conclusion that emerges from the reactivity measurements and agglomeration modelling is that alternative ways of gasification, such as entrained flow gasification, has to be considered for gasification of Victorian brown coal.

Table of Contents

1. Introduction

This six-month project followed from another research project assessing fundamental behaviour of brown coals during gasification at low temperatures to 900°C. The work under the current project, funded by the Brown Coal Innovation Australia (BCIA), included the following aspects:

- Thermodynamic modelling to predict agglomeration behaviour of Victorian brown coal during gasification – in particular under temperature range relevant to fluidized bed conditions
- Preparation and testing of a number of catalysts for volatile cracking, gas cleaning and water gas shift reaction and carbon conversion. These catalysts are to include power station flyash, and Nickel Oxide and Iron Oxide supported on Char, Al_2O_3 and SiO_2.

In addition to the above, the work also included a comparison of gasification reactivity of four Victorian brown coals and a Rhenish lignite obtained from RWE of Germany. This was carried out in thermo-gravimetric analyser under CO_2 and steam gasification atmospheres.

2. Experimental work

The experimental work involved the design and construction of a range of reactors, and use of commercial instruments. These are briefly described in the following sections.

2.1 Quartz reactors

Two types of reactors were used - a reactor, that can be used in both fixed bed and fluidized bed mode; a second type of reactor of drop-tube type was also used.

2.1.1 Fixed-bed fluidized bed reactor

The quartz reactor consists of two operating zones separated by a quartz frit. An important feature of this two-stage reactor is that it allows one to study the interactions between volatiles and char, and their effects on the volatilisation behaviour of AAEM species during pyrolysis. When required, the top zone can operate as a fixed bed and the bottom zone as a fluidised bed. Therefore, this reactor is in fact two reactors connected in tandem. Figure 1 shows the schematic diagram of the reactor, adapted from Quyn et al [1]

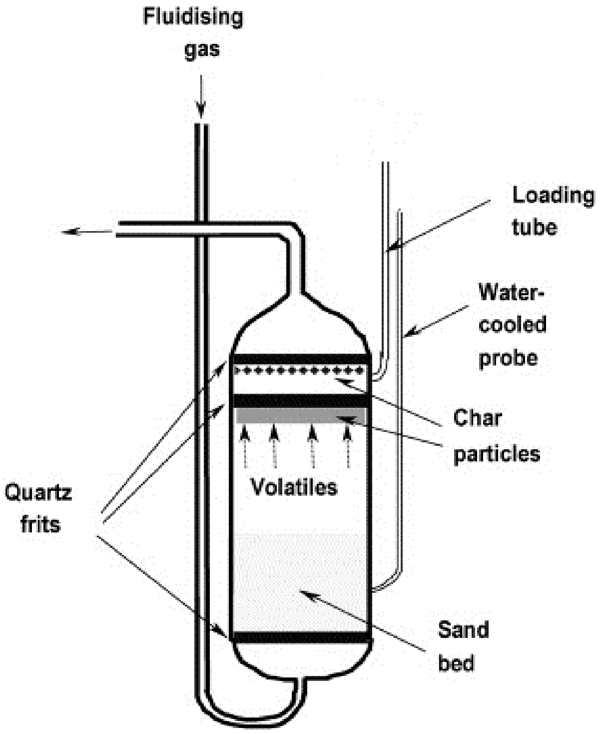
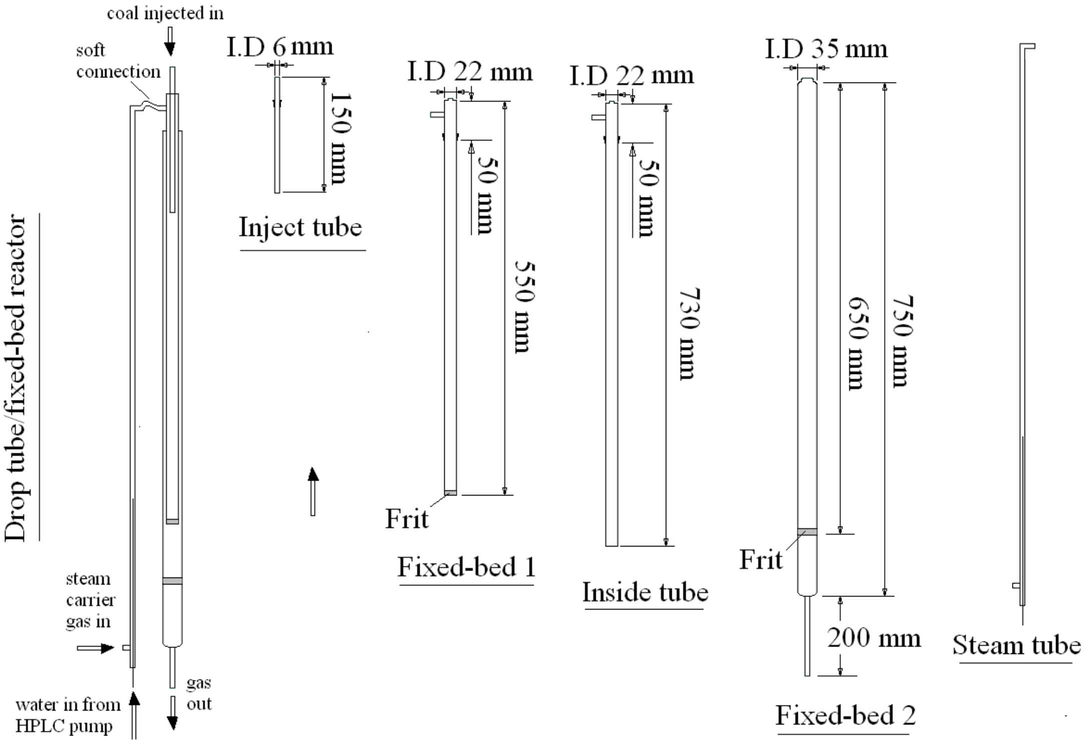


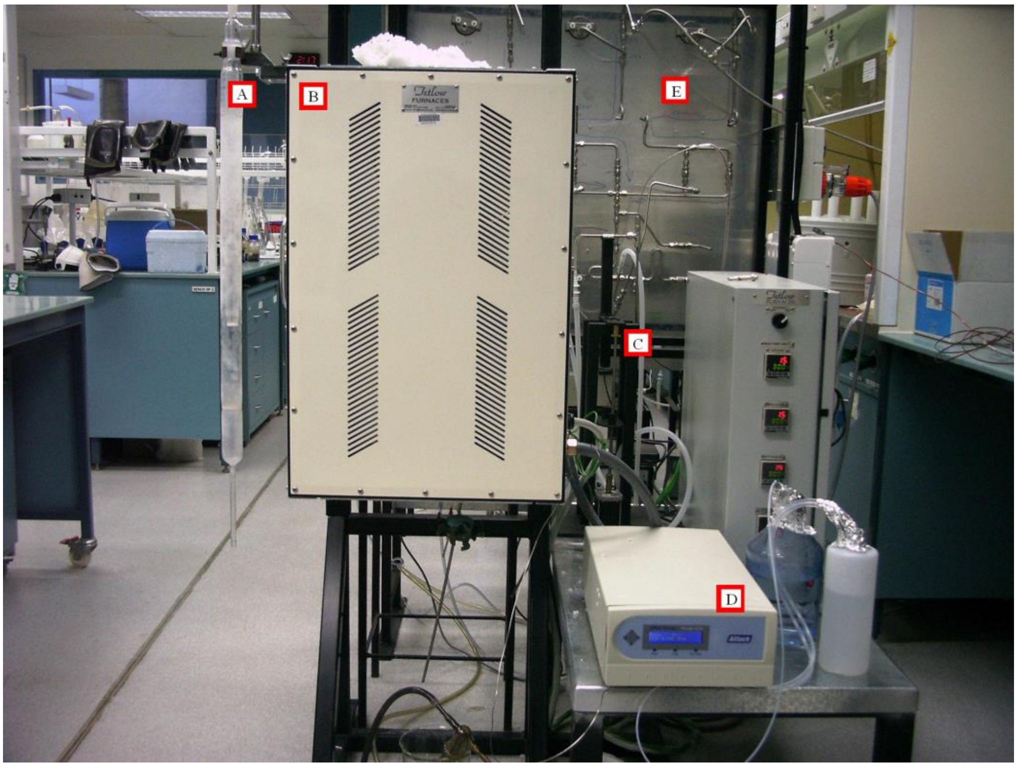
Figure 1 : Schematic diagram of the reactor that can be operated in fixed bed or fluidized bed mode

2.1.2 Drop tube-fixed bed reactor

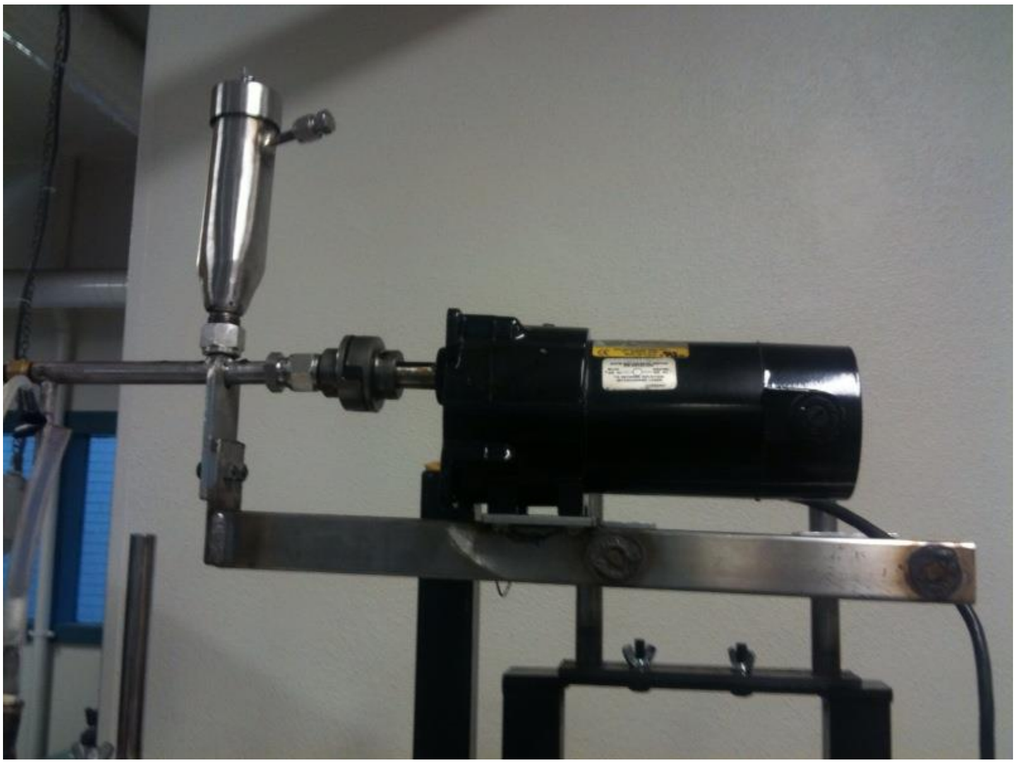
This reactor is also made of quartz. It consists of a drop tube reactor placed above a fixed bed reactor. Figure 2-a shows schematic diagram of the reactor. The coal together with the steam and gases were injected from the top of the reactor. The char remains on the top frit and the volatiles are further pushed down. When catalyst is placed on the lower frit, it could work as a fixed bed of catalysts for the volatiles that pass through. Figure 2-b shows a photograph of the experimental setup. In the photograph, A is the drop tube-fixed bed reactor, B is the three-zone furnace (which provides the external heat), C is the coal feeder, D is the HPLC pump which pumps the water for the steam generation purpose, and E is the panel with the mass flow controllers, pressure gauges, etc. installed on it.



(a) Reactor drawings



(b) Experimental setup in lab



(c) The screw feeder on top of the reactor

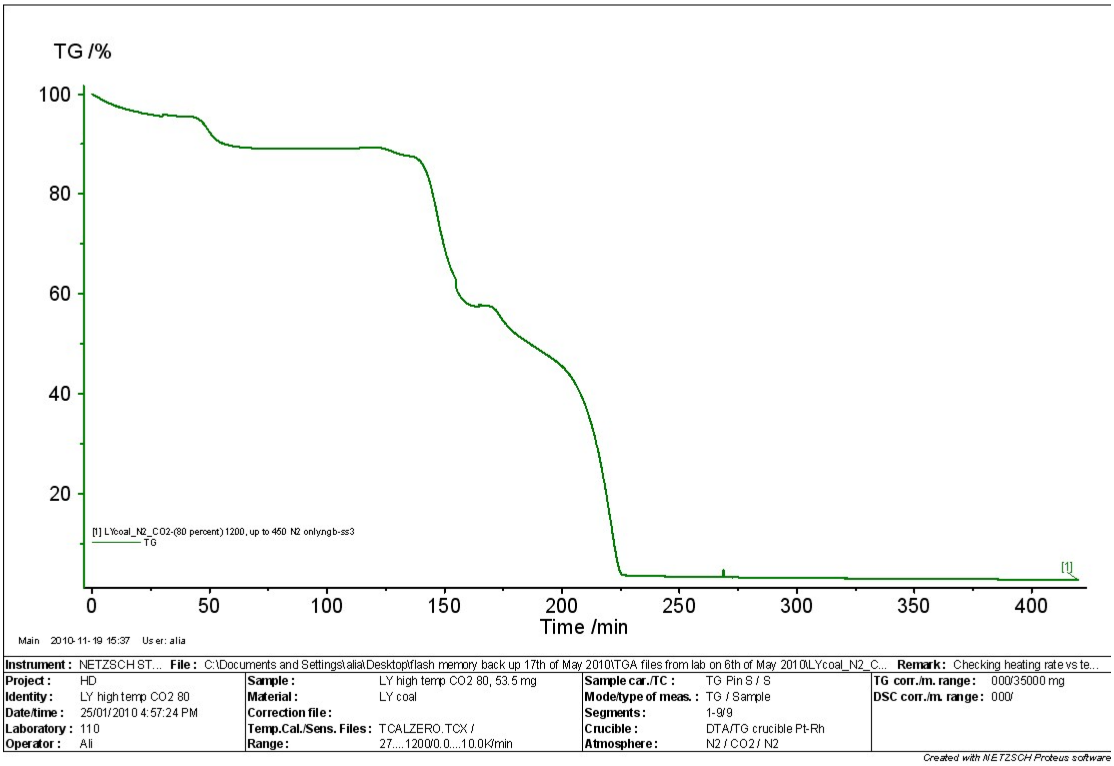
Figure 2. The reactor system.

2.2 Thermogravimetric Analayser (TGA)

The TGA used is of 449 F3 Jupiter type with a dedicated steam-injection system. The temperature can be raised up to 1250°C and the heating rate can be set between 5 K/min and 40 K/min.

2.2.1 Analysis of coal pyrolysis and gasification using TGA

The char is generated from the coal in a reactor first, and then the char is analysed using the TGA. In few experiments coal, instead of char, was directly used within the TGA. Different gas environment, such as Nitrogen, Carbon Monoxide, Oxygen, steam, and/or mixture of these gases can be introduced in the TGA. Figure 3 shows a typical weight loss curve from the instrument.



Instrument : NETZSCH ST... **File :** C:\Documents and Settings\alia\Desktop\flash memory back up 17th of May 2010\TGA files from lab on 6th of May 2010\LYcoal_N2_C... **Remark :** Checking heating rate vs te...

Project :	HD	**Sample :**	LY high temp CO2 80, 53.5 mg	**Sample car./TC :**	TG Pin S / S	**TG corr./m. range :**	000/35000 mg
Identity :	LY high temp CO2 80	**Material :**	LY coal	**Mode/type of meas. :**	TG / Sample	**DSC corr./m. range :**	000/
Date/time :	25/01/2010 4:57:24 PM	**Correction file :**		**Segments :**	1-9/9		
Laboratory :	110	**Temp.Cal./Sens. Files :**	TCALZERO.TCX /	**Crucible :**	DTA/TG crucible Pt-Rh		
Operator :	Ali	**Range :**	27....1200/0.0....10.0K/min	**Atmosphere :**	N2 / CO2 / N2		

Figure 3 , Typical weight loss curve (Loy Yang Coal, CO_2 and N_2 gas mixture)

2.3 Catalysts used

2.3.1 Iron

Various forms of iron have been reported as the catalysts for coal gasification reactions, pyrolysis, and tar decomposition. According to Tamhankar et al. [2], metallic iron (reduced form) catalysts have higher activity for benzene decomposition and selectivity for methane formation than iron oxides. Iron can be deactivated rapidly in the absence of hydrogen due to coke deposition.

Yu et al. [3-5] investigated the effects of iron on the steam gasification of brown coal and a novel char-supported iron catalyst for the water-gas-shift reaction. It was found that the hydrogen yield can be increased significantly by using iron as catalyst to promote gasification and the water-gas-shift reaction. Both reduced-iron (α-Fe and γ-Fe) and magnetite (Fe_3O_4) were highly dispersed in a char to enhance the gasification rate and the hydrogen yield. Nordgreen et al. [6,7] used metallic iron as a catalyst for tar elimination during the atmospheric pressure gasification of biomass. It was claimed that elemental iron had high activity for tar reforming. The yields of CO, CO_2, and H_2 are increased, the yield of CH_4 is decreased and the tar content is reduced. The activity of metallic iron is enhanced with increasing temperature. Compared with iron oxides, the capability of metallic iron to break tar is extremely high. Furthermore, Matsuoka et al. [8] studied the effects of nonporous silica sand, porous γ-alumina and iron oxide-impregnated porous γ-alumina on the gas products during the steam reforming of woody biomass. It was detected that iron oxide promoted the yield of H_2, especially at higher temperatures. They claimed that the effect of iron oxide on the yield of H_2 of coke reforming was insignificant. A redox reaction of iron oxide is the predominant pathway for forming H_2. The iron oxide was reduced by CO produced during the steam reforming process. Then, the reduced iron oxide reacted with steam to produce H_2.

2.3.2 Nickel

Ni-based catalysts are widely used in the petrochemical industry for reforming processes. The components of normal Ni-based catalysts are Ni element, support materials and prompters, controlling the activities of Ni-based catalysts [9]. Alumina is usually used as the support material to enhance the mechanical strength of the catalysts and AAEM are used as promoters [10, 11]. Ni-based catalysts have high activity for tar removal and increase syngas yield. They are however expensive and easily deactivated because of irreversible loss of surface area, coke deposition and poisoning. Coke deposition and poisoning on catalyst active sites are the main drawbacks of Ni-based catalysts. Zhang et al. [12] investigated the effects of three Ni-based catalysts (ICI46-1, Z409 and RZ409) on tar breakdown. It was found that the conversion of heavy tars was higher than 99%. The yield of H_2 increased by 6–11 vol%(db). With elevating temperature, the yield of H_2 was enhanced and the yield of light hydrocarbons was dropped.

Courson et al. [13] developed a new Ni–based catalyst for dry reforming of methane. The results showed that nickel oxide has interaction with the support. The catalysts which were prepared at 1100 ℃ and contained 2.8 wt% Ni exhibit the best activity.

Some researchers have changed their focus to other novel metal catalysts that are able to keep high efficiency on removing tar, because the Ni-based catalysts are deactivated significantly by carbon deposition. Tomishige et al. [14] compared the activities of the $M/CeO_2/SiO_2$ (M=Rh, Pd, Pt, Ru, Ni) catalysts on tar removal during cedar wood gasification. The order of catalyst activity at 823K was the following: Rh>Pd>Pt>Ni>Ru. The tar conversion of the $Rh/CeO_2/SiO_2$ catalyst was about 88%

at 823 K and jumped to the 97% at 873 K. In addition, Asadullah et al. [15-17] researched on the performance of the Rh/CeO_2/M (M=SiO_2, Al_2O_3, and ZrO_2) catalysts for gasification in a continuous feeding fluidized-bed reactor. The authors found that the Rh/CeO2/SiO2 exhibits the best performance for producing syngas or hydrogen. The Rh/CeO2 catalyst was deactivated when the surface area dropped from 60 to 13m^2/g in the continuous feeding system and its activity can be maintained by loading CeO_2 on the high-surface-area SiO_2. These catalysts show high activity, but they are expensive and have regeneration problems. Therefore, they are not suitable for industrial application.

2.3.3 Catalyst preparation

In our experiments, we assessed the following catalysts:

- pure iron oxide
- pure nickel oxide
- char supported iron
- char supported nickel
- alumina supported iron, and
- alumina supported nickel catalysts
- Flyash from Yallourn power station – supplied by TRUenergy

Loy Yang coal from Victoria was used to prepare the char-based catalyst. The coal's ultimate analysis results (on dry basis) are: Carbon- 65%; Oxygen- 25.5%; Hydrogen- 4.6%; Nitrogen- 0.72%, Sulfur- 0.50%, Chlorine- 0.11%. The coal was first crushed and sieved. Those with the size range of 106-150 µm were acid-washed. The reason for acid-washing the coal is to ensure that all the minerals are washed off. In order to acid-wash the coal, the coal was stirred in diluted (1 Molar) HNO_3 for twenty four hours. It was then filtered and washed until neutrality washed liquid was obtained.

The acid-washed coal was then stirred in $Fe(NO_3)_2$ or $Ni(NO_3)_2$ solution for 24 hours. Nitrogen was fed in the stirring flask during the twenty four hour stirring period. The slurry of the impregnated coal was then filtered and washed with deionised water. After sieving, this coal was gasified at 800 ºC in 10% steam for 30 minutes, in order to generate the char-based catalyst. The iron and nickel content in the supported catalyst is 1.1 wt% (dry basis).

In the case of alumina supported catalysts, alumina particles of 106-150 µm size range were stirred in $Fe(NO_3)_2$ or $Ni(NO_3)_2$ solution on a hot plate so that the solution evaporates gradually. The alumina particles were then separated using a centrifuge. The impregnated particles were then dried and sieved.

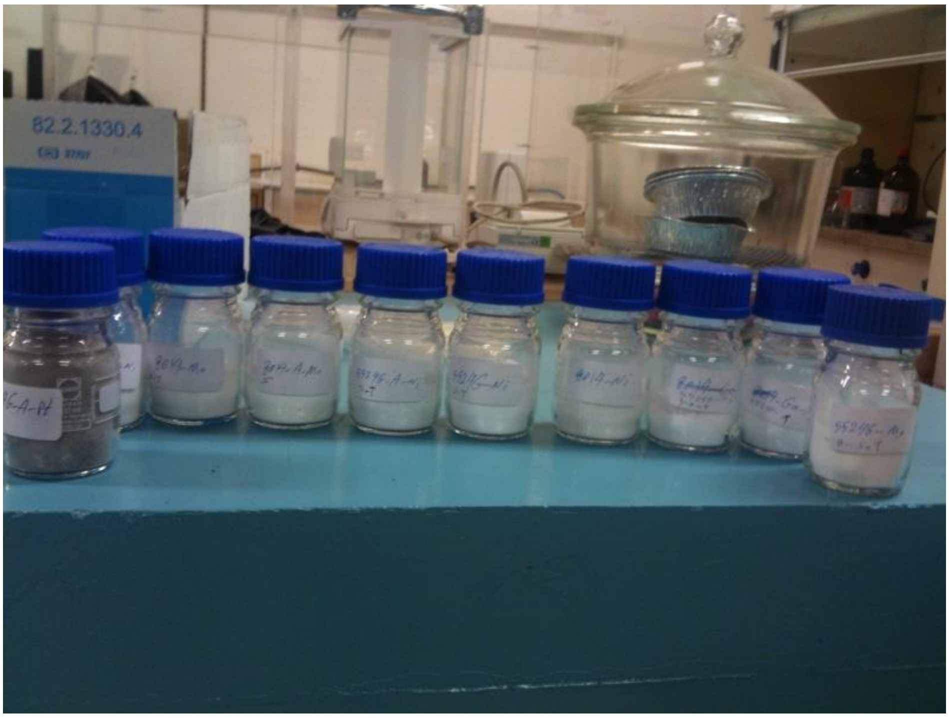


Figure xx – Catalysts prepared for the shift reaction

2.4 Coals used

Four different Victorian brown coals and one German brown coal provided by the RWE were used in the study. The CHNS analysis was employed to detect whether acid washing or the 0.1 nickel impregnation has an effect on the coal composition. Moreover, it can provide further explanation for catalytic effects on reactivity. The following table shows the ultimate analysis of the different coals after different pre-treatment.

Table 1: CHNS Analysis from different brown coals in wt % on a dry basis

Sample	Pretreatment	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
German lignite	Raw coal	61.10	4.40	0.68	0.57	27.55
	HNO_3 washing	62.53	4.53	0.77	0.45	26.02
	0.1 Ni^{2+}	61.68	4.31	0.93	0.36	27.02
Anglesea	Raw coal	57.97	3.68	1.32	2.77	30.45
	HNO_3 washing	64.20	4.30	0.79	3.60	26.20
	0.1 Ni^{2+}	58.81	3.96	1.44	1.05	33.84
Loy Yang	Raw coal	61.20	4.08	1.83	0.29	28.89
	HNO_3 washing	61.90	4.40	0.68	0.50	26.90
	0.1 Ni^{2+}	56.97	4.14	1.42	0.34	31.43
Maddingley	Raw coal	53.20	3.49	1.12	2.08	27.72
	HNO_3 washing	60.50	4.30	0.70	3.10	26.20
	0.1 Ni^{2+}	55.70	3.61	1.36	0.56	33.57
Yallourn	Raw coal	60.29	3.77	0.96	0.26	32.52
	HNO_3 washing	63.90	4.20	0.69	0.20	30.50
	0.1 Ni^{2+}	56.77	4.05	1.19	0.29	37.10

By comparing the carbon content of German raw coal, with the acid washed and the 0.1 Ni^{2+} impregnated samples, there are only slight differences, which lied in the sensitivity of the instrument (±3%). All the other values of hydrogen, nitrogen and sulphur are in a comparable range. For Loy Yang and Yallourn brown coal, the acid washing removes some carbon. All other values stay in a comparable range.

For Maddingley and Anglesea brown coals the carbon content increases. It is assumed that the decrease was caused by the instrument error or by the decrease of sulphur content from the coal samples, whose inorganic formed was removed during the acid washing and impregnation. However, this was not observed for the other samples. Therefore, further investigation need to be done in the future.

The oxygen concentration alters with the carbon concentration. The mineral matter was also measured. The mineral matter is known to significantly affect the reactivity.

To have an idea how many and what species are inherent in the investigated brown coals, their ash contents were analysed. The facilities for this analysis were not available, thus the tests were done by an external institute. The following table shows the oxides left in the ash after burning the coals.

Table 2: Oxide in ash in wt % on a dry basis of the investigate brown coals

Sample	German lignite	Anglesea brown coal	Loy Yang brown coal	Maddingley brown coal	Yallourn brown coal
Ash yield	5.7	3.8	3.7	12.4	2.2
SiO_2	14.30	7.1	56.5	17.3	2.1
Al_2O_3	1.90	14.0	20.5	15.6	1.0
Fe_2O_3	11.87	27.3	4.6	25.0	47.6
TiO_2	0.41	0.2	1.5	0.1	0.1
K_2O	0.47	0.4	1.3	0.3	0.2
MgO	13.36	12.1	3.6	6.7	17.2
Na_2O	3.90	3.0	4.7	4.8	3.0
CaO	30.01	11.7	1.6	12.1	11.6
SO_3	19.95	24.7	5.0	20.4	19.6
P_2O_5	0.01	<0.1	0.2	0.1	<0.1

Table 2 points out that Maddingley brown coal has by far the highest ash yield, what means the highest mineral matter concentration. For the reactivity it is very important what kinds of minerals are inherent in the coal. Therefore, the total ash content is only a poor indicator for the reactivity. [22] Silicon has hardly an effect, whereas calcium is a very catalytic active species. German lignite, for example, should be among the more reactive coals, due to the high amount of calcium and iron. Whereas Loy Yang brown coal should have the lowest reactivity, because it contains mainly silicon and aluminium, which have no catalytic effect. [4, 24]

To prove the efficiency of the acid washing, one investigated the ash content once more after acid washing. The following table shows the oxides left in the ash after burning the acid washed coals.

Table 3: Oxide in ash in wt % on a dry basis after acid washing

Sample	Anglesea brown coal	Loy Yang brown coal	Maddingley brown coal	Yallourn brown coal
Ash yield	0.9	5.7	5.2	0.6
SiO_2	21.9	80.2	39.8	6.5
Al_2O_3	14.9	13.4	31.1	2.5
Fe_2O_3	51.8	1.6	29.0	78.3
TiO_2	0.60	1.37	0.13	0.35
K_2O	0.60	1.55	0.17	0.16
MgO	1.4	0.4	0.4	1.6
Na_2O	1.4	0.5	1.6	2.7
CaO	2.9	0.1	0.5	2.1
SO_3	4.7	0.0	1.1	7.0
P_2O_5	0.1	0.1	0.1	0.1

One can see from Table 3 that the 1 molar HNO_3 washing reduces significantly the mineral matter content. The ash content decreased by 60 % for Anglesea, Maddingley and Yallourn brown coal. For Loy Yang brown coal, the ash content slightly increased. Especially magnesium and calcium components were nearly removed completely by acid washing. As a consequence, the reactivity is expected to decrease drastically, because those two components have a strong catalytic effect. Moreover, acid washing acted like a desulfurization by reducing the sulphur content for all investigated brown coals by far beyond 50 %.

2.5 Experimental Procedure

2.5.1 Gasification Experiments

In the gasification experiments, the reactor is weighed before the experiments. It is then placed in the furnace. The flow-rates of the gases are preset on the mass flow meters beforehand. When the furnace reaches the desired temperature, coal feeding, gas injection and steam injection are started at the same time. The product gas from the reactor passes through two stages of coolers, a bed of silica gels and also particle filters. It then passes through a micro-GC which measures the gas composition.

After the experiment, the amount of coal fed to the system is measured and the weight of the reactor with char is measured. From the difference and ultimate analysis of the coal and char samples, char-conversion can be determined.

2.5.2 Water-Gas-Shift experiments

The water gas shift reaction experiments were performed in a fixed bed of catalysts. Based on a number of preliminary tests, around 1.1 grams of were loaded in the reactor. The reactor was then placed in the furnace and the desired temperature was achieved. The flow rates of the gases (CO, Argon) as well as the water for the system were all preset. The product gas from the reactor passes through two stages of coolers, a bed of silica gels and also particle filters, and finally through a micro-GC which measures the gas composition.

3. Results and Discussion

3.1 O_2 and steam gasification

We designed two series of experiments at 800 ^{0}C with two levels of coal feeding rates of 100 mg/min and 25 mg/min. These experiments include pyrolysis in Ar atmosphere (condition 1); gasification in 3000 ppm O2 balanced with Ar (condition 2), 15% steam balanced with Ar (condition 3) and 3000 ppm O_2 plus 15% steam balanced with Ar (condition 4). The char yields and coal conversion were calculated and shown as in Figure 4 and Figure 5.

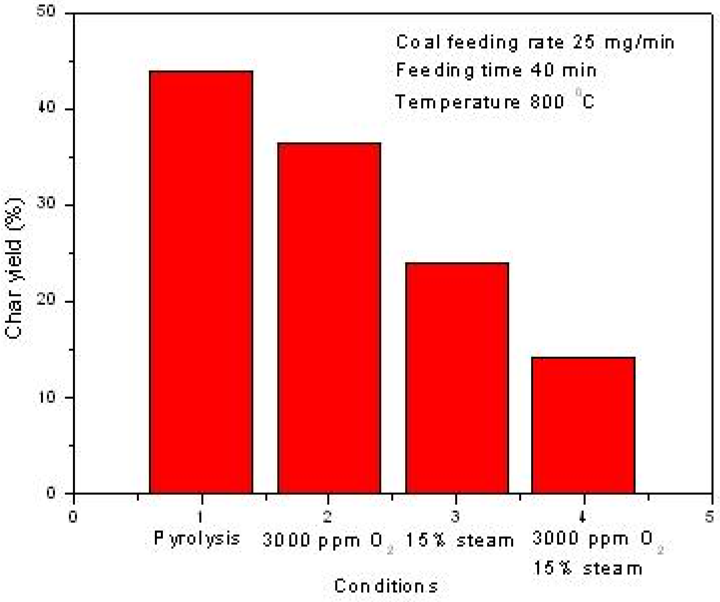


Figure 4 Char yields in different experimental conditions

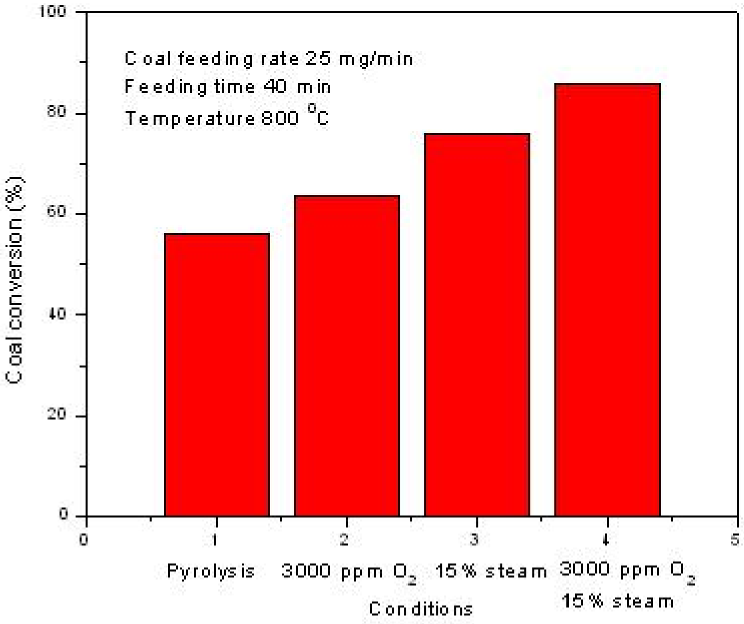


Figure 5 Total coal conversions in different conditions

From Figure 4 and Figure 5, it can be seen that the char yield or coal conversion is much different under different conditions. The net coal conversions during gasification equal the total coal conversions minus the coal conversion in pyrolysis, as shown in Figure 6.

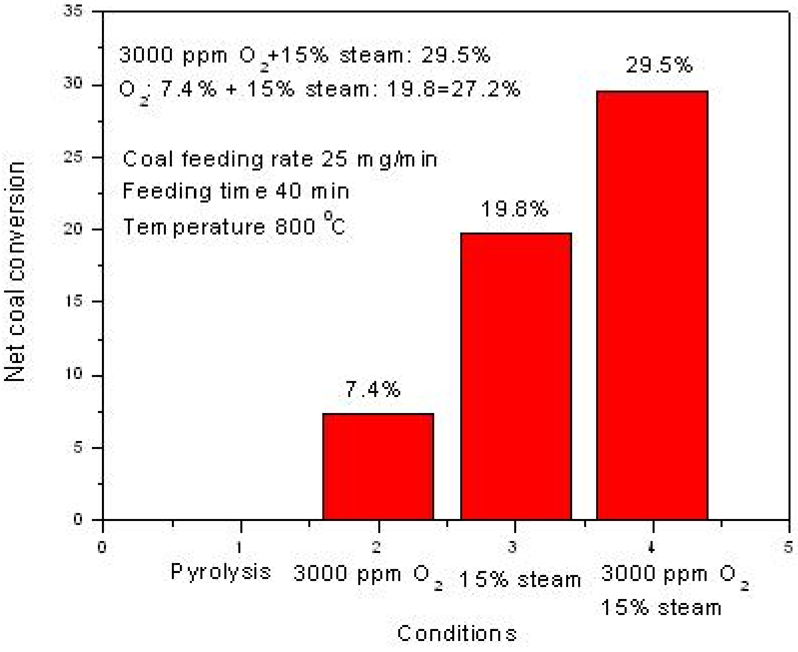


Figure 6 Net coal conversions in different conditions

According to the same way, we can conclude the net coal conversions at coal feeding rate with 100 mg/min for conditions 1 to 4 shown in Figure 7.

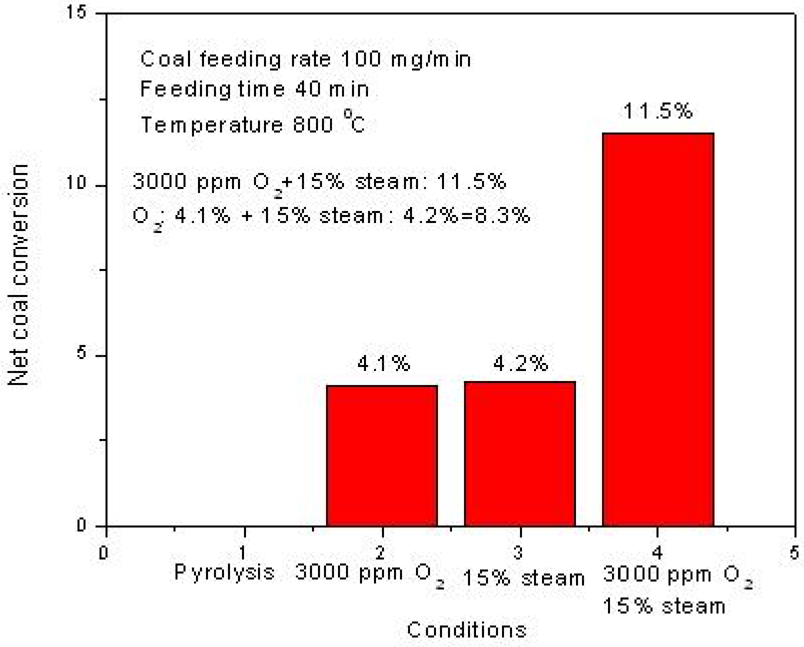


Figure 7 Net coal conversions during gasification at different conditions – 100mg/min feeding rate

Figure 6 and Figure 7 show that the net coal conversions for 3000 ppm O_2 plus 15% steam at feeding rates of 25 mg/min and 100 mg/min both are higher than that in singular gasification using 3000 ppm O_2 or 15% steam respectively. The results also demonstrate the effect of varying coal feeding rate

3.2 Effects of coal feeding rate, coal feeding time and holding time on char yields for 3000 ppm O_2 balanced with Ar

Experiments by changing feeding rate by 25 mg/min, 50 mg/min, 75 mg/min and 100 mg/min were conducted. As expected and shown in Figure 8, with the increase of coal feeding rate, the char yield slightly increased. Because the volatile concentration at higher coal feeding rate is higher than that in lower coal feeding rate, more amount of oxygen reacted with volatile and less amount of oxygen reacted with char, which resulted in the increase of char yield.

When coal feeding rate was fixed, changing feeding time by 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, we can see from Figure 9 the char yield kept almost same. It can be explained that during the feeding time, oxygen was consumed with volatile while raw coal thermal cracking and without or very less remaining oxygen reacted with nascent char.

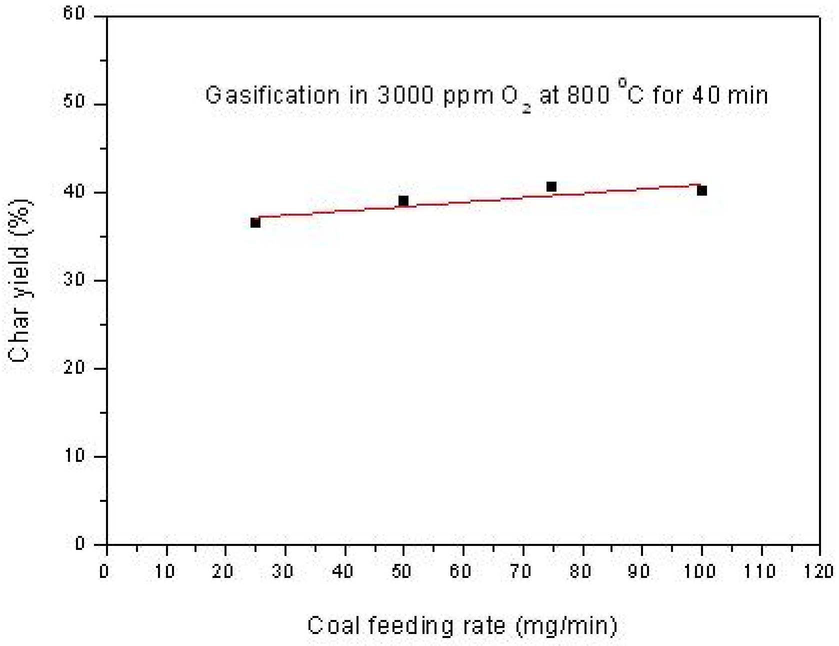


Figure 8 Char yields in different coal feeding rate with 40 min feeding time

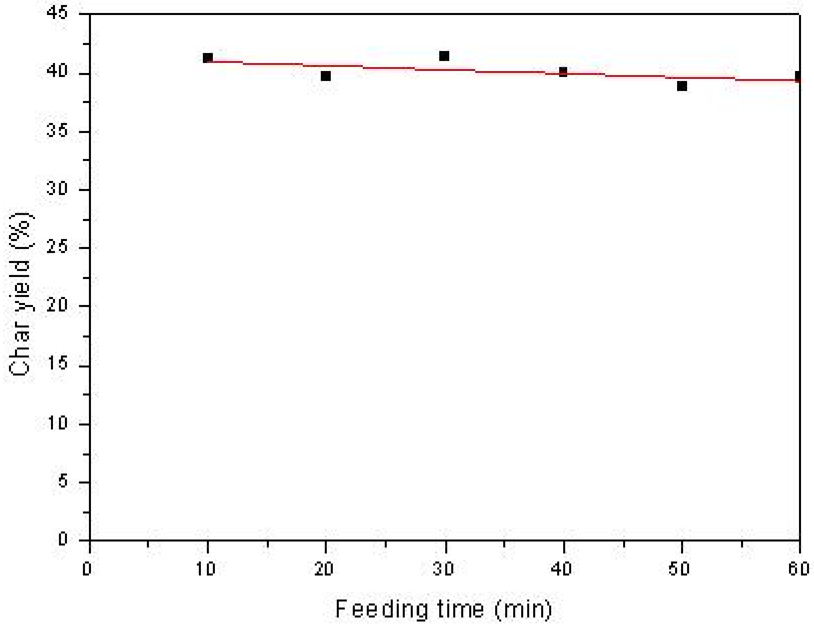


Figure 9 Char yield as a function of feeding time at feeding rate of 100 mg/min

However, when the holding time increased from 0, 10 min, 20 min, 30 min to 40 min, we can find from Figure 10 that the char yield decreased gradually, albeit very slowly. This means only when oxygen completed reacting with volatiles, it reacted with char further. For relatively large sample mass used in the experiments, the reaction was controlled by diffusion, after a certain time, outer layer around char was totally ashed slowing diffusion of reactants to the inner core. That is why significant reduction of char yield took place.

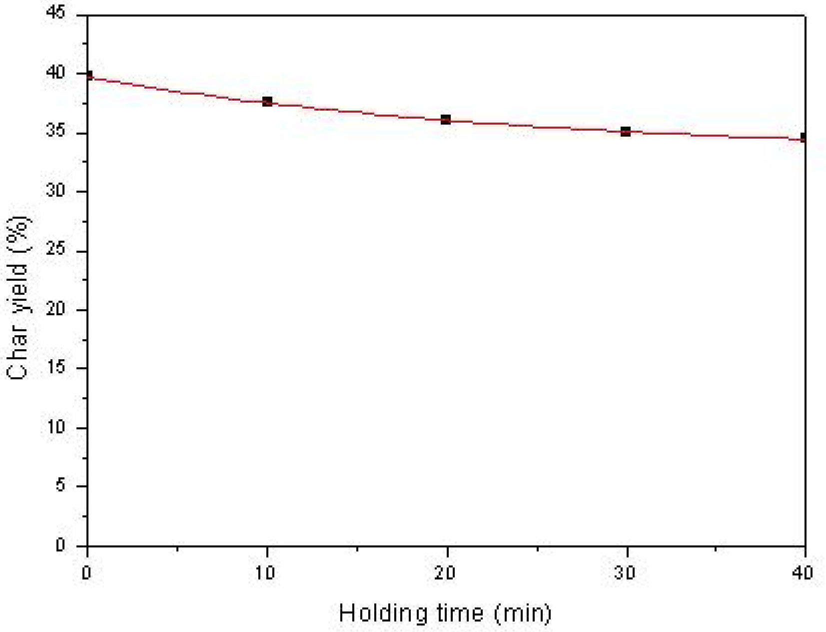


Figure 10 Char yield in different holding time after 40 min gasification

3.3 Char reactivity by TGA

Two main groups of results presented here. One is related to the experiments in which the char is generated in fluidized bed/fixed bed reactor under different conditions. The other group is related to the experiments in which char is generated from the coal in the TGA.

In the experiments in the first group parameters such as effects of gas environment, coal feeding time during the gasification, coal feeding rate during the gasification, holding time during gasification are studied.

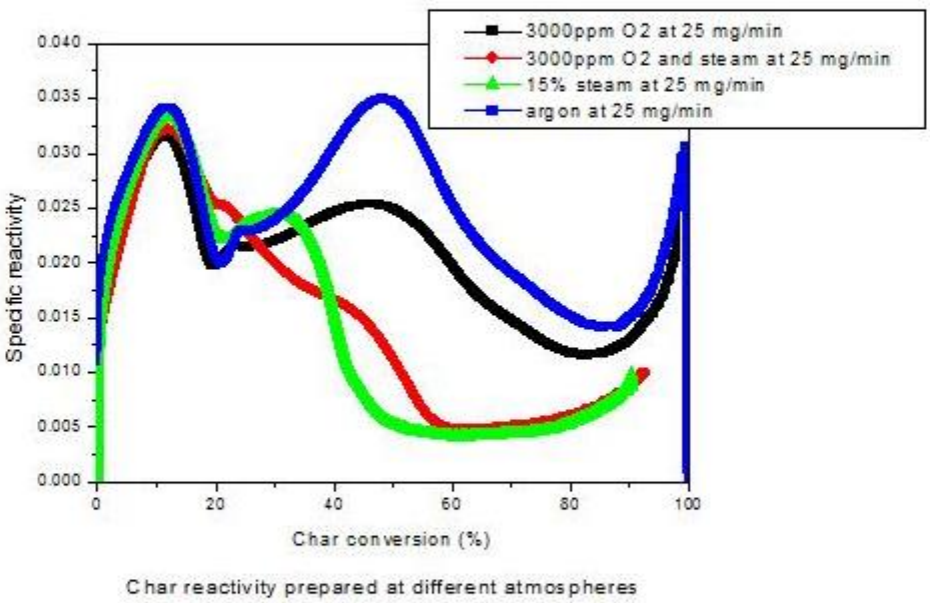


Figure 11 Reactivity for char prepared at different gasifying agents at feeding rate of 25 mg/min

Figure 11 shows that at feeding rate of 25 mg/min, for different gasifying agents, char reactivity exhibited different changes. For pyrolysis in argon and gasification in 3000 ppm O_2, the char reactivity curves have two peaks. During steam gasification, the second peak of char reactivity tended to disappear.

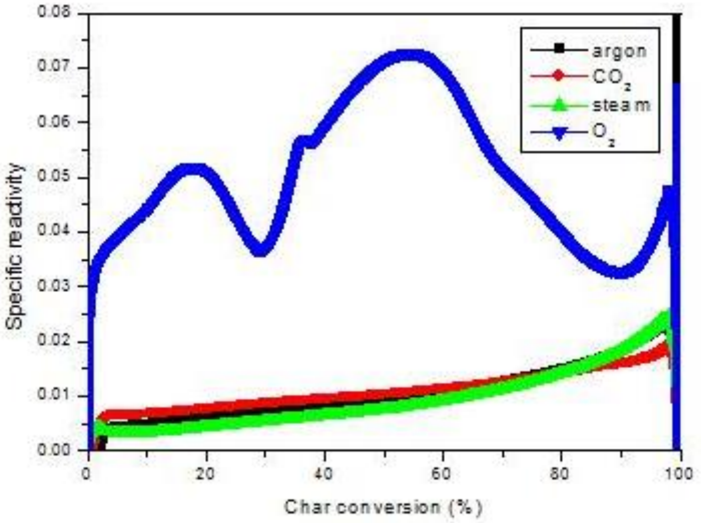


Figure 12 Reactivity for char prepared at different gasifying agents at feeding rate 100 mg/min

Figure 12 shows that at feeding rate of 100 mg/min, the char reactivity exhibited different trend from that at feeding rate of 25 mg/min. Because high concentration of volatile was produced at 100 mg/min, the volatile-char interaction may cause the change of char reactivity. Char reactivities at pyrolysis in argon, gasificatin in CO_2 or in 15% steam exhibited the same shape and level. However, after gasifying at 3000 ppm O_2, the char reactivity is much higher than other conditions. This is because oxygen can eliminate the volatile-char interaction, making the char of higher reactivity.

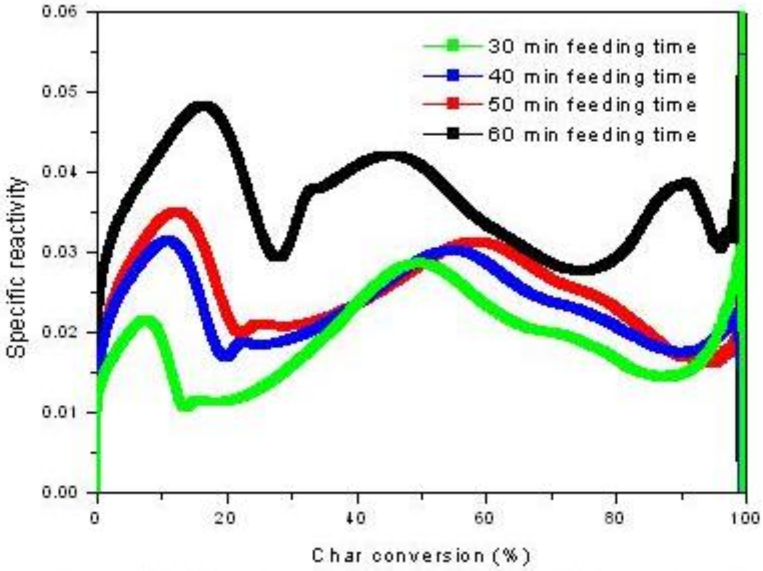


Figure 13 Reactivity for char prepared at different feeding time at 100 mg/min feeding rate for gasification 3000 ppm O_2

Figure 13 shows that char reactivity at different feeding time when coal feeding rate was at 100 mg/min. With longer feeding time, the char reactivity would be higher. This is because longer residence time in reactor for nascent char could have more chance to react with oxygen, which may eliminate the volatile-char effect.

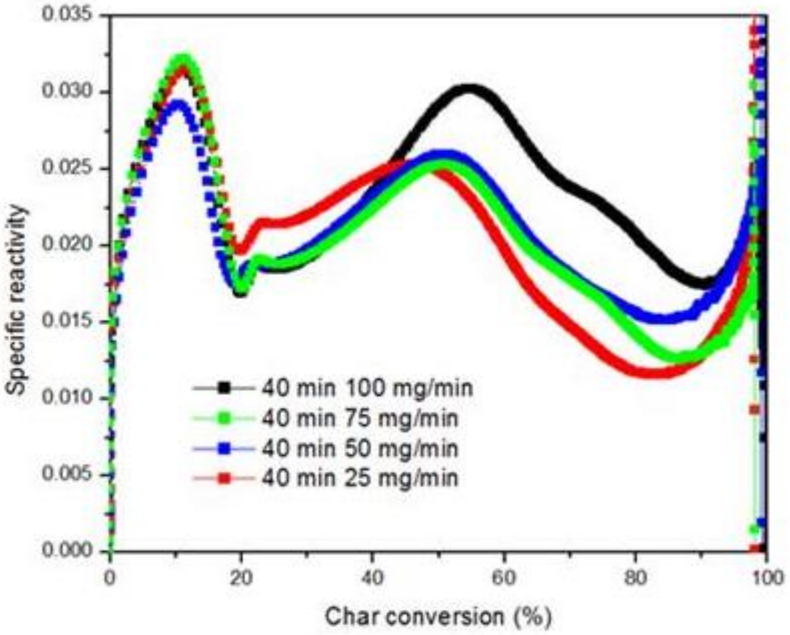


Figure 14 Reactivity for char prepared at different coal feeding rate

Figure 15 shows that char reactivity did not exhibit much change while changing coal feeding rate. The shapes of curves are very similar and the magnitude of reactivity is also around the same level. The reason is because oxygen was almost consumed while volatiles were released from raw coal during pyrolysis or thermal cracking.

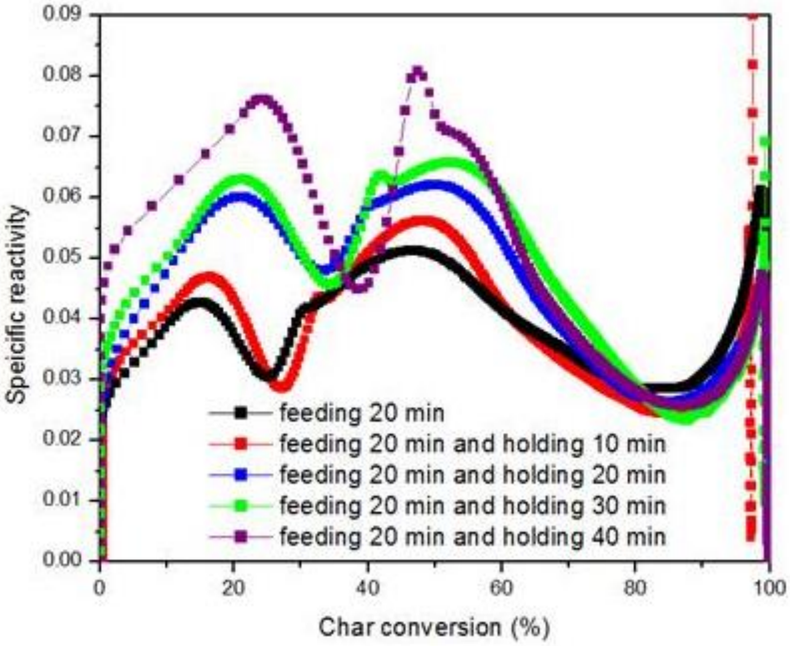


Figure 15 Reactivity for char prepared at different holding time

However, with the increase of holding time from 10 min to 40 min after 20 min gasification in 3000 ppm O_2, char reactivity could be further increased. This is because oxygen reacted with char in a longer time, and then the surface of char could make more change.

In the second group of experiments reactivity studies were conducted using a 449 F3 Jupiter Thermogravimetric Analayser (TGA). Around 10 mg of coal was homogeneously spread over the bottom of a crucible. The temperature programming was to increase the temperature up to 105 ºC, and then run the system isothermally at 105 ºC for 30 minutes. This was to ensure complete drying of the coal. The system was then heated up, to 450 ºC, in presence of only N2 in the system. This was the stage at which the other gases, e.g. CO2 and/or steam, were introduced to the system. Then the system was heated up to 1200 ºC with a heating rate of 10 ºC/min. The weight recording was continued for about 2 hours after the system reached 1200 ºC.

The curves of coal conversion and reactivity versus temperature for different types of coal and in different gas composition are shown in Figures Conv vs Temp (a-c) and Reactivity vs Temp (a-c)

Conversion is determined by equation (1)

$$Conversion = \frac{(m_i - m_t)}{m_i} \times 100 \qquad (1)$$

Coal reactivity in gasification environment is studied using TGA. The reactivity is determined by equation (2)

$$R_{coal} = \frac{-1}{(m_{i,coal} - m_{ash})} \frac{dm}{dt} \qquad (2)$$

Where, $m_{i,coal}$ is the initial mass of the coal; mash is the ash mass formed after reaction, and dm/dt is the measured mass loss rate.

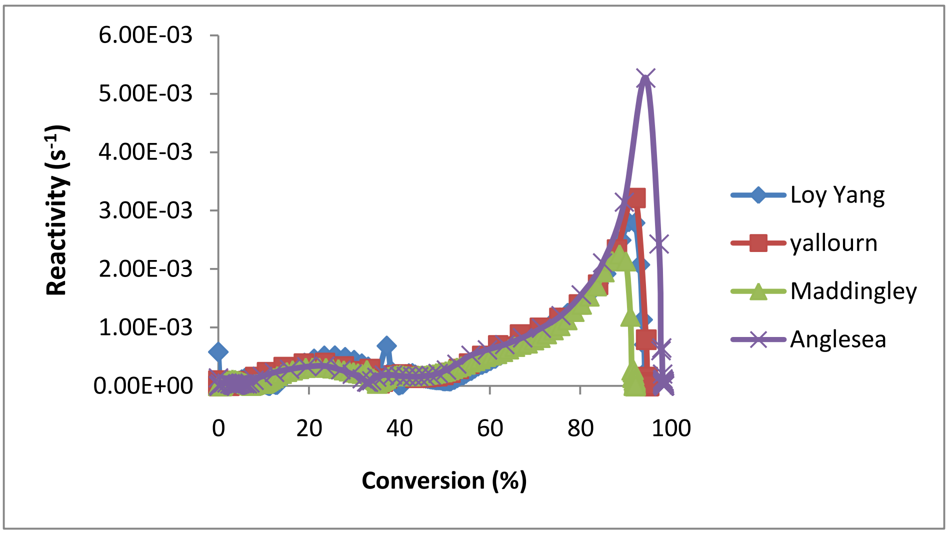


Figure 16 Reactivity variation with conversion for different types of Victorian Coal, 20% CO_2 in N_2

Figures 16, 17, and 18 demonstrate the variation of reactivity of four different types of coal with conversion, for different gasification environments. It can be observed that the reactivity peak occurs at lower conversions, when the CO_2 concentration is increased, as well as when steam is added.

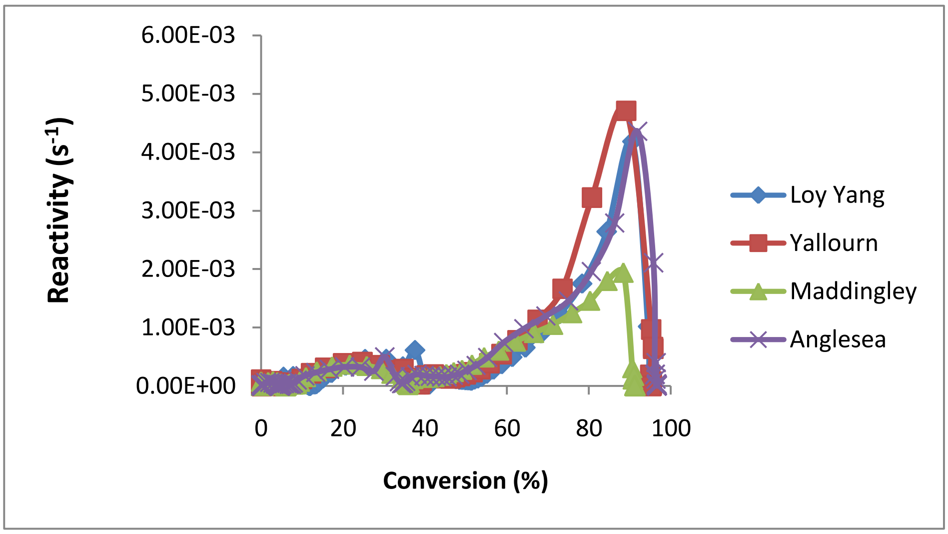


Figure 17 Reactivity variation with conversion for different types of Victorian Coal, 40% CO_2 in N_2

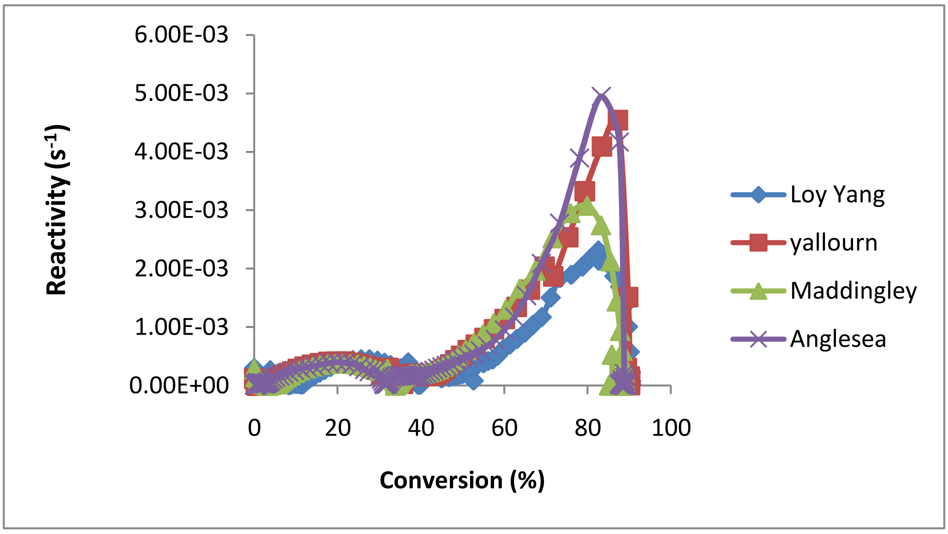


Figure 18 Reactivity variation with conversion for different types of Victorian Coal, 20% CO_2 +15% steam in N_2

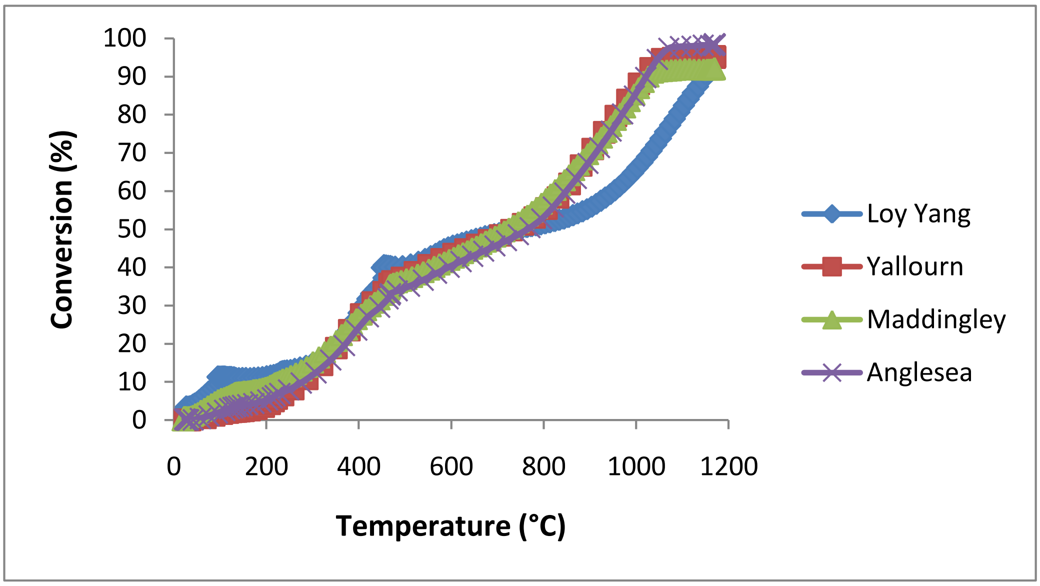


Figure 19 Variation of conversion with temperature, four different Victorian coals, 20% CO_2 in N_2

Figures 19, 20, and 21 demonstrate the variation of conversion with temperature for four different types of Victorian Coal. It is evident from Figure 19 that all coals need temperatures higher than 1000°C for high C-conversion. This temperature is within the agglomeration/sintering zone, therefore running the gasification within that temperature zone by using 20% CO_2 only is not feasible. This means, alternative ways of gasification, such as entrained flow gasification has to be considered for gasification of Victorian brown coal. CO_2 is introduced at 450 °C onwards; however, the trend would not change even if CO_2 was introduced right from the beginning.

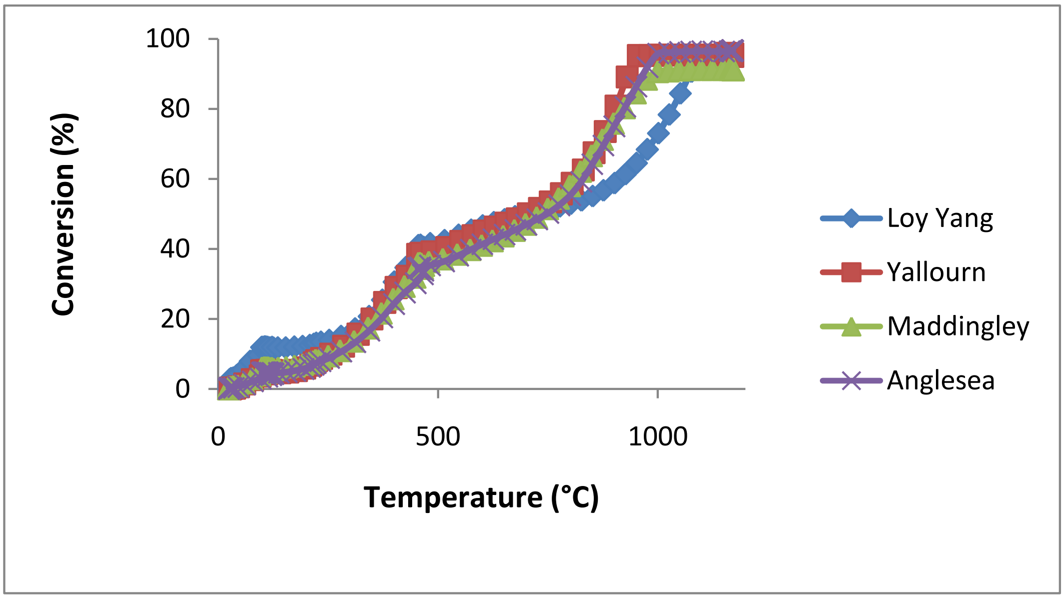


Figure 20 Conversion variation with temperature, four different Victorian coals, 40% CO_2 in N_2

Figure 20 shows that Loy Yang coal follows same trend as before, so increasing the CO_2 content for gasification would not be sufficient in order to achieve high C-conversion. However, the other three coals require lower temperature than before

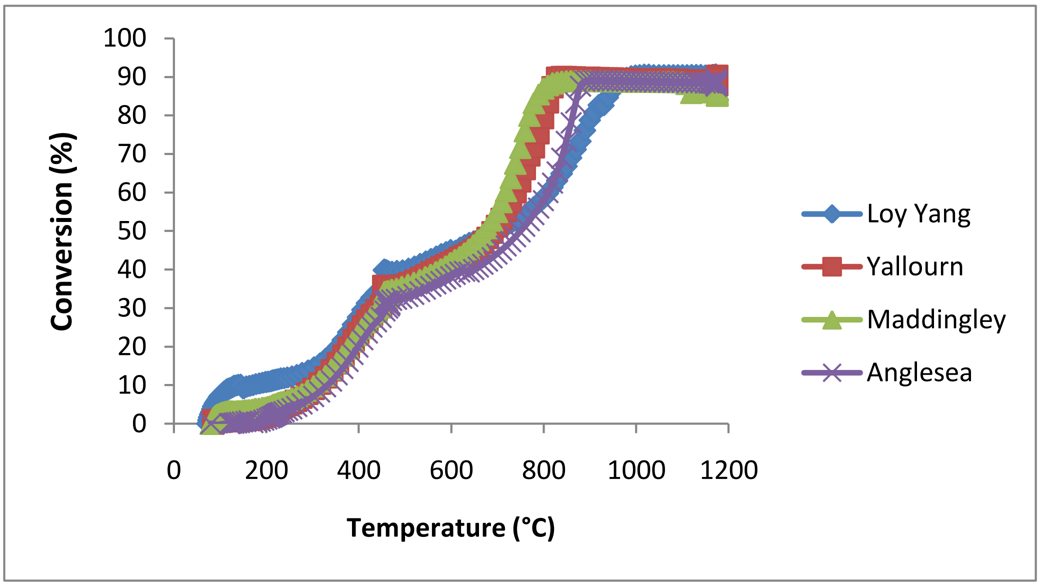


Figure 21 Conversion variation with temperature, four different Victorian coals 20% CO_2 +15% steam in N_2

It can be observed in Figure 21 that the addition of steam, decreases the required temperature for high conversion, rather considerably for most of the coals. Loy Yang coal, however, still needs high temperature to achieve high conversion. This could be due to the structure and/or the coal/ash composition. Addition of a catalytic compound can be a solution to tackle this problem and decrease the temperature required for Loy Yang coal to achieve high conversion.

3.4. Effect of added catalysts on gasification reactivity of coal

3.4.1 Gasification with 20 % CO_2

The comparison experiments of raw coals, acid-washed coals and impregnated coals were carried out in TGA in order to investigate the catalytic effect of $Ni(NO_3)_2$ and $Fe(NO_3)_3$ in CO_2 gasification reaction. Moreover, the temperature associated to the maximum reactivity and burnout temperatures were compared. Acid washing removes most parts of the inorganic minerals from the coal, which have a catalytic effect on the gasification. [19] The removal of the inorganic mineral matter content can be verified by comparing the reactivity of acid washed coal with raw coal. After impregnating the acid washed coal samples, it can be obviously seen that a certain compound catalytically affects on the C-CO_2 gasification reaction. [19, 20] In the following part the reactivity of the investigated brown coal are plotted against temperature after different pre-treatment. It cannot alienate the results of one coal to another, because of the big differences between coals, as explained in the introduction. The sharp peaks of all samples in the temperature range from around 150 to 200 ºC are due to the start of the CO_2 insert and the resulting short amplitude of the balance arm.

3.4.1.1 Reactivity of German lignite

The following chart shows the reactivity of German lignite against temperature.

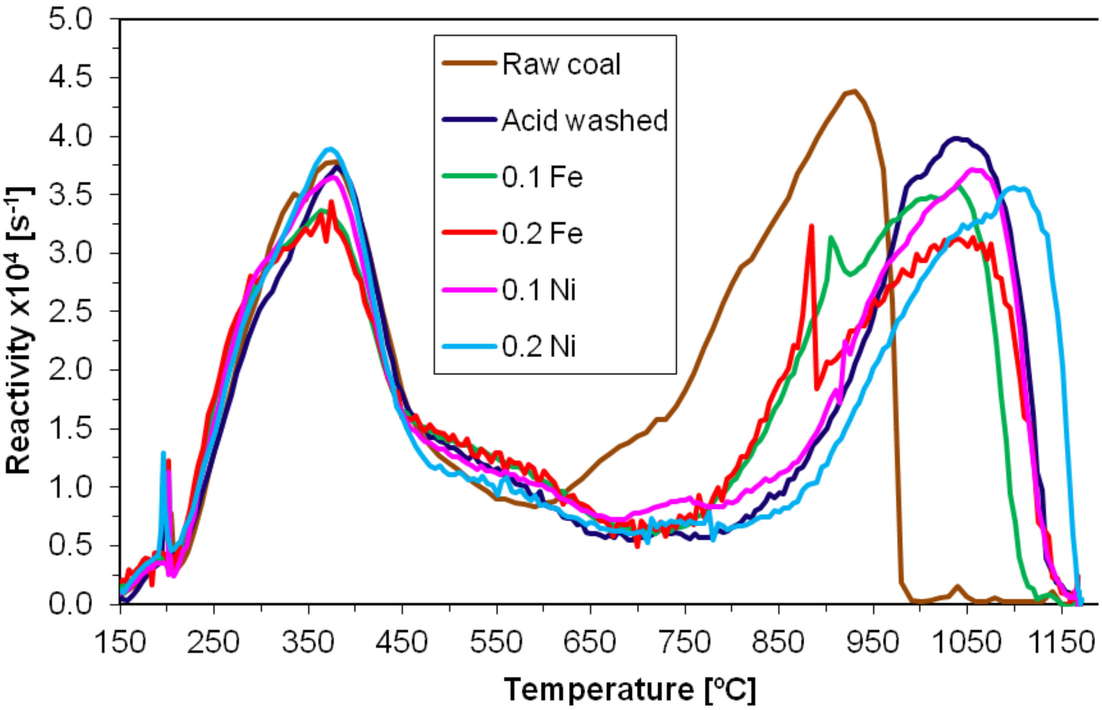


Figure 22: Reactivity of German lignite on CO_2 gasification after different pre-treatment

In the low temperature range up to approximately 600 ºC all samples shows nearly the same reactivity. The fist peak is mainly due to devolatilization of volatiles. Neither acid washing, nor ion solution impregnation has any noticeable effect on the volatile content. The second appearing peak is caused by the gasification reaction of carbon with carbon dioxide. The gasification reaction takes place in the range between 800°C to 1150ºC.

By comparing the maximum reactivity of the raw coal and the acid washed coal, it can be recognized that acid washing reduces the reactivity of the German lignite, because acid solution washes away most active catalytic species. [19] Not only the maximum reactivity, but also the temperature of the maximum peak is shifted after acid washing towards higher temperature, due to the lack of mineral matter. Moreover, the burnout temperature of the raw coal is around 150 ºC lower. This means that the gasification of the raw coal completes before the acid washed coal has reached its maximum.

The curves of the impregnated samples are still lower than the raw coal sample, because the alkali and alkaline metallic species, promote the gasification together, however, have been removed during acid washing; therefore the reactivity still reduced after impregnated with extra Fe and Ni ions. The maximum reactivity with nickel impregnation is slightly higher and a little bit shifted to higher temperatures. A higher nickel concentration is even harmful, the reactivity slightly decreases and is shifted to higher temperatures.

The sharp peak at around 870 ºC of the 0.2 M Fe impregnated curve and the little sharp peak in the same region of the 0.1 M Fe impregnated are due to reactions of iron with CO_2. For 0.2 Fe the peak is stronger developed, because more iron is existent. The reaction enthalpy is approximately 120 kJ/mol, which means 50 kJ/mol lower than those of carbon with CO_2. [22] As a result the reactivity of the iron impregnated samples start to rise at lower temperatures compared to the others. After all iron has reacted, the reactivity drops, which causes the sharp peak.

As a whole, a conclusion can be drawn that neither Ni^{2+} nor Fe^{3+} catalyses the gasification of German brown coal. This, however, require further investigation.

3.4.1.2 Reactivity of Anglesea brown coal

The reactivity of Anglesea brown coal shows huge differences to those of the German lignite in the temperature range higher than 650 ºC. In the region below 650 ºC it delivers similar results due to the effects discussed above.

The following plot shows the reactivity of Anglesea brown coal after different treatment against temperature.

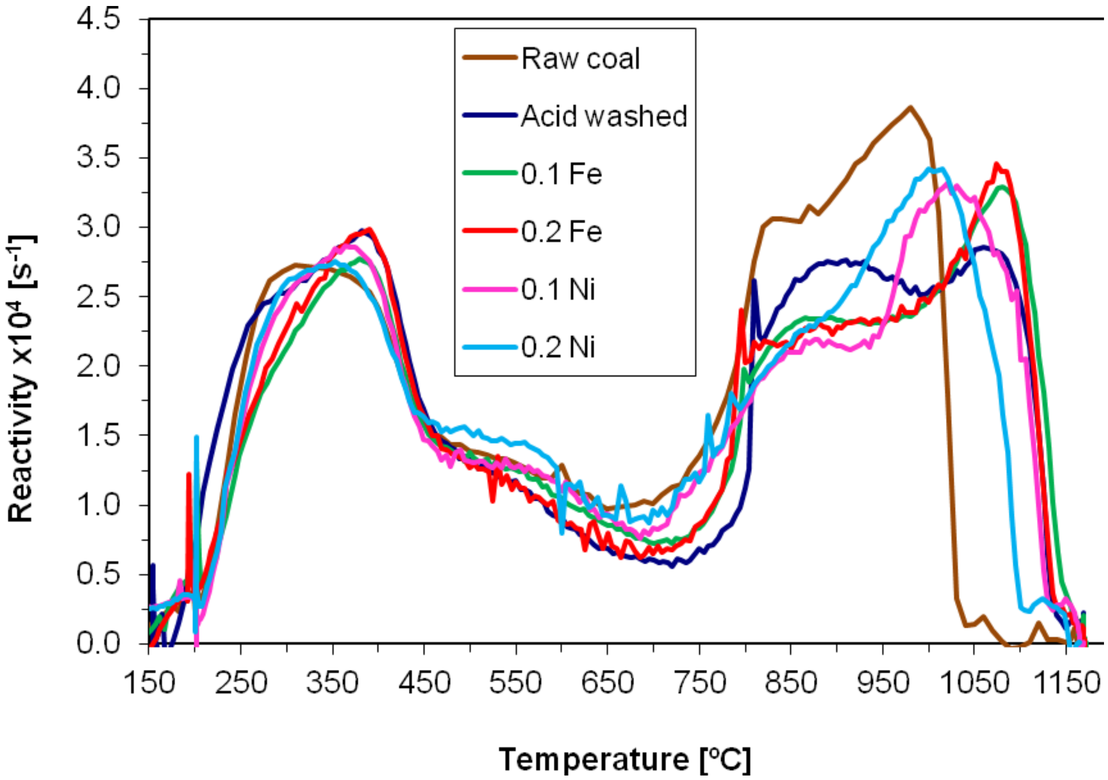


Figure 23: Reactivity of Anglesea brown coal on CO_2 gasification after different pretreatment

It is noticeable that all curves show broad peaks in the gasification temperature range. For example raw coal has a big shoulder at around 820 till 870 °C. This shoulder may be caused by the high iron content of the raw coal. As shown in Table 2, Anglesea brown coal has the highest iron content after Yallourn brown coal. As mentioned above, the reaction of iron with carbon dioxide has a lower reaction enthalpy, which means that this reaction can take place at lower temperatures than the carbon with CO_2 reaction. Even after acid washing one can see a sharp peak at 805 °C, cause by the iron reaction. Acid washing reduces the reactivity, because it removes inherent minerals. It cannot completely remove all minerals, that is why the sharp peak appears in the acid washed curve. The ash yield is reduced from 3.8 % to 0.9 % by acid washing, which means that most minerals were removed. The maximum reactivity decreased by 25 % and the associated temperature increased by 80 °C. Moreover, the burnout temperature of the raw coal is about 100 °C lower. The nickel impregnated coals do not show the sharp peak maybe due to the substitution of iron compounds with nickel.

In general, all impregnated curves present a higher maximum reactivity than the acid washed coal. Nevertheless, they are still lower as the raw coal, because impregnated single catalyst cannot replace all removed minerals and their catalytic effect. The 0.2 M $Fe(NO_3)_3$ impregnation has a slightly better effect compared to the 0.1. By comparing the burnout temperature, only the nickel impregnations deliver an improvement. The 0.2 Ni curve displays the best results. It increases the maximum reactivity by 20 % and reduces the burnout temperature by 40 ºC.

3.4.1.3 Reactivity of Loy Yang brown coal

The following figure 24 shows the reactivity of Loy Yang brown coal on CO_2 gasification.

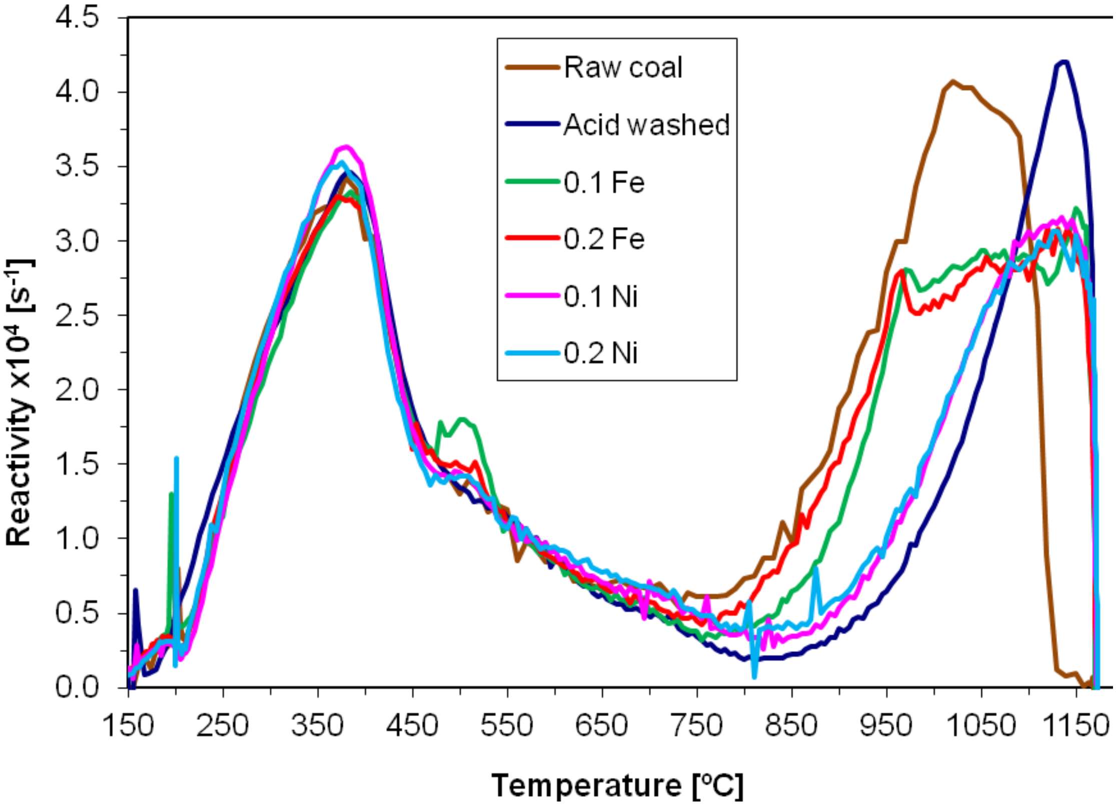


Figure 24: Reactivity of Loy Yang brown coal on CO_2 gasification after different pre-treatment

As figure 24 shows, there is no significant difference in the maximum reactivity in the low temperature range. Except the little peak from 0.1 Fe at around 500 ºC the samples behave in a same way until 750 ºC. The reactivity of the iron impregnated samples starts to increase earlier than the others. This fact is caused by the reaction of iron with CO_2. As mentioned in chapter 0, the reactions of iron with CO_2 have a lower reaction enthalpy that is why those curves start to raise at lower temperatures. Although the gasification starts earlier, the reactions do not complete earlier, because in the beginning mostly iron is reacting. Moreover, their reactivity peaks towards CO_2 gasification are broader and not so high as the one of the raw coal. Furthermore, the impregnation with 0.1 M $Fe(NO_3)_3$ delivers a better result than the 0.2 molar iron impregnation.

Nickel impregnation does not have catalytic effects on the reaction, the reactivity value is even less than that after acid washing. The nickel curves follow the acid washed curve over a long track, but have a lower peak value at 1100 ºC.

The maximum reactivity after acid washing increased compared to the raw coal. Moreover, the associated temperature is increased for about 100 ºC. Table 2 clarifies that Loy Yang brown coal mainly contains silicon, which has almost no catalytic effect and very little of other components. The remove of most minerals, by HNO_3 washing delivers no huge difference, because most removed minerals are non-catalytic active ones. As a consequence, acid washed and raw coal does not show dramatic difference like the other investigated brown coals. The slight increase in reactivity is because the peak of acid washed curve is very narrow. That means that most carbon reacts at a certain temperature instead of over a wide temperature range. This situation is not favoured, because this means that the reaction is hard to control, due to the sudden commencement.

Another important evaluation factor is the burnout temperature. On the one hand all impregnated samples show the same burnout temperature like the acid washed. On the other hand the raw coal reaches that temperature already 40 ºC earlier. Moreover, the reactivity after acid washing starts to rise at 850 ºC, whereas the raw coal curve rises at 750 ºC.

3.4.1.4 Reactivity of Maddingley brown coal

The reactivity of Maddingley brown coal delivers similar results in the low temperature range like the previous coals. In the CO_2 gasification region, however, it shows some serious differences compared to the previously discussed brown coals. Figure 25 shows the reactivity of Maddingley brown coal after different treatment against temperature.

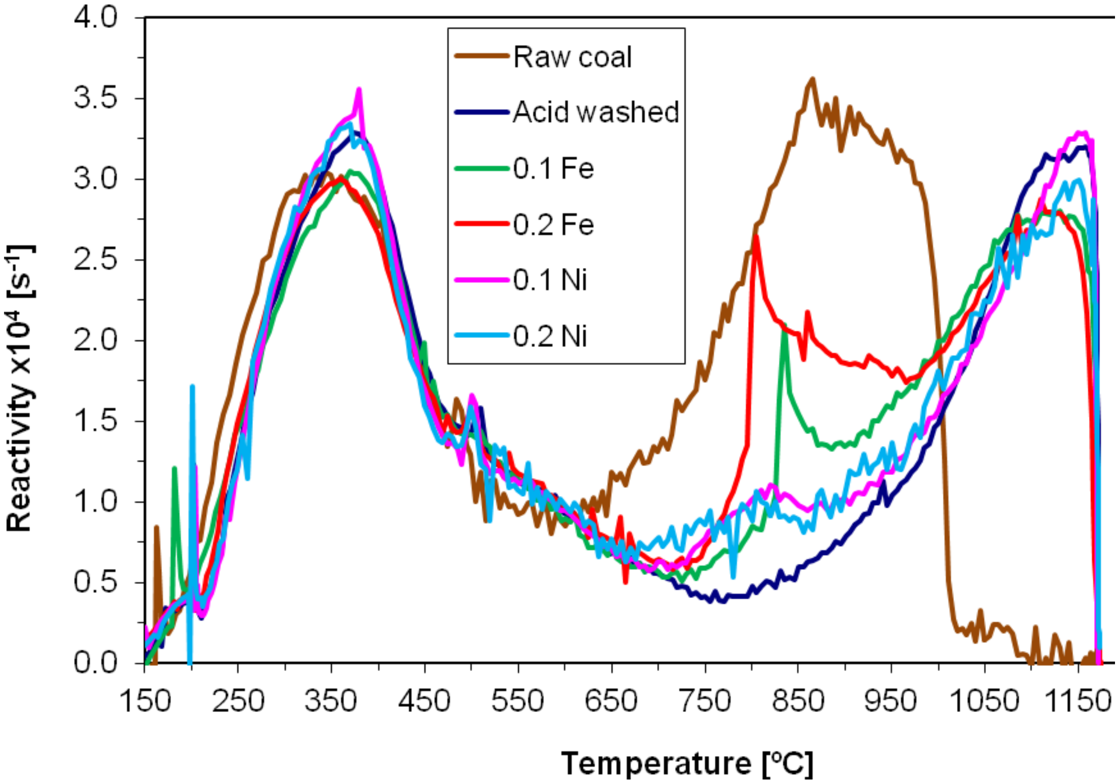


Figure 25: Reactivity of Maddingley brown coal on CO_2 gasification after different pre-treatment

First of all, the raw coal peak is very broad and has its maximum value nearly 300 ºC earlier than the acid washed coal. Because Maddingley brown coal has a very high ash yield and contains a large amount of iron, iron and CO_2 reactions play an important role for the raw coal reactivity. Furthermore, the iron impregnated curve shows three maxima. The second maxima at 805 and 835 ºC, respectively, is due to the already mentioned reaction of iron with CO_2. In this case the iron reaction peak is very strongly developed for the impregnated ones. That is the reason for the high necessary temperature to reach the maximum reactivity. Thus the reactivity peak at the lower temperature was corresponding to the Iron carbonation reaction. Moreover, the maximum reactivity is even a bit lower, so overall the iron impregnation is even harmful for the reactivity.

By comparing the acid washed with the raw coal, it can be seen a significant increase of the temperature of the maximum reactivity. The maximum reactivity itself decreases only slightly, but the compulsory temperature and especially the burnout temperature increase drastically.

Regarding the nickel impregnation curves, nickel hardly delivers any effect on the reactivity. The impregnation with 0.1 M $Ni(NO_3)_2$ delivers slightly better results, but both concentration have nearly the same effect.

3.4.1.5 Reactivity of Yallourn brown coal

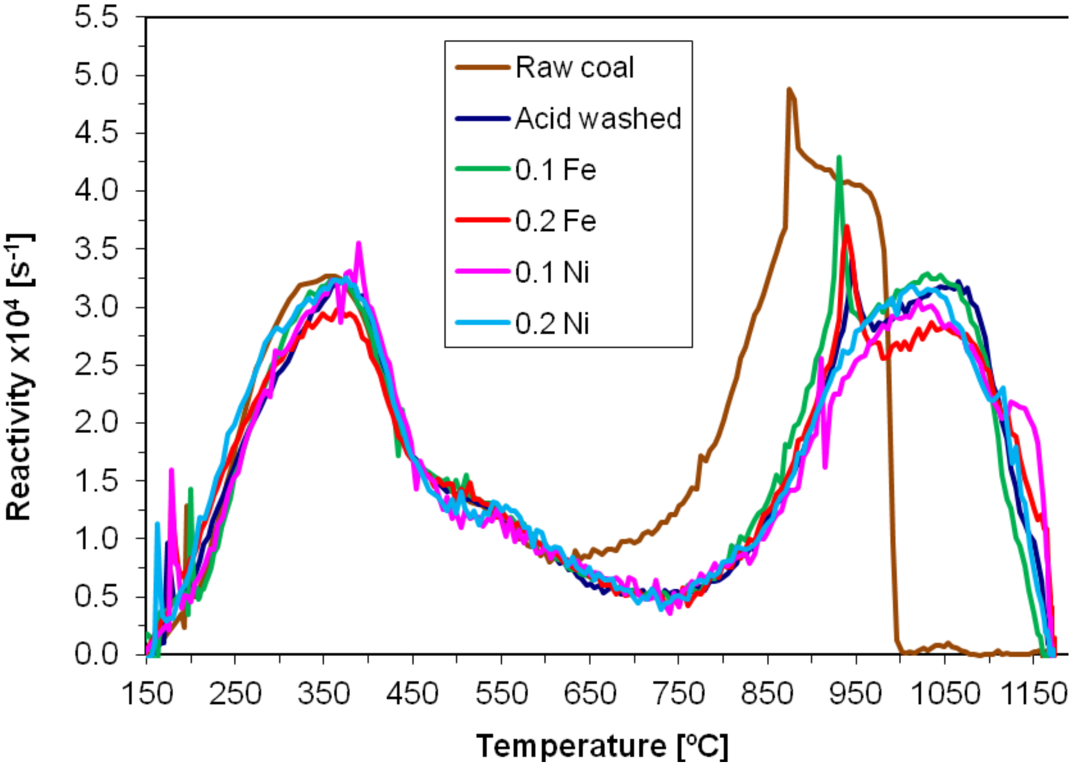


Figure 26: Reactivity of Yallourn brown coal on CO_2 gasification after different retreatment

In Figure 26, the first part is similar to that of the other brown coals. The special behaviour of Yallourn brown coal is that all curves, except the nickel impregnated ones, show a sharp peak before the large peak in the gasification range. Not only the iron impregnated, like the other brown coals, but also the acid washed and the raw coal feature that sharp peak. Yallourn brown coal contains a lot of iron, as stated in Table 2. That is the reason for the appearance of the sharp peak also in the reactivity curve of the raw coal. Anglesea brown coal shows only a shoulder, because it contains less iron. Acid washing can only remove most minerals, but not all, for this reason even acid washed coal shows a small sharp peak. The nickel impregnated coals do not show the sharp peak maybe due to the substitution of iron compounds with nickel.

Although a peak of the iron in the acid washed coal reactivity is still visitable, the acid washing was really successful. Not only the maximum reactivity dropped for roughly

35 % but also the associated temperature increased for 170 ºC. Moreover, the burnout temperature of the raw coal is 160 ºC lower than those of the others.

Like all other investigated brown coal, neither iron, nor nickel nitrate impregnation has a positive catalytic effect on the CO_2 gasification.

3.4.1.6 Summary of 20 % CO_2 gasification

The CO_2 gasification causes for all samples a two-peak distribution. The first peak, in a temperature range between 250 and 450 ºC is due to devolatilization of volatiles. The peak in the temperature region of approximately 750 until 1150 ºC is caused by the gasification reaction of carbon with CO_2.

In the low temperature range up to approximately 600 ºC all brown coal samples shows nearly the same reactivity. Neither acid washing, nor ion solution impregnation has any effect on the volatile content. That is why the reactivity in this region is nearly unaffected. But the gasification reaction is strongly dependent on the pre-treatment.

The acid washing with 1 molar HNO_3 reduces significantly the reactivity of all investigated brown coals due to the removal of most inorganic minerals. [27] After the acid treatment the maximum reactivity decreased and the associated temperature increased. Without catalyst a higher activation energy for the reaction of carbon with carbon dioxide is required. For this reason more char is left for higher temperature reactions and the maximum reactivity occurs at higher temperatures. Furthermore, the burnout temperature increased for most coals for over 100 ºC. The only exception is Loy Yang brown coal, whose maximum reactivity increased. Loy Yang brown coal contains mainly catalytic inactive mineral species, like silicon and aluminium. As a consequence, Loy Yang´s reactivity is not strongly dependant on the mineral matter content. Furthermore, the peak in the gasification range became much narrower, which lead to the increase of the reactivity.

The maximum reactivity of the iron or nickel impregnated samples is still lower than those of the raw coal, because impregnation catalytic effect cannot compete with the inherent mineral species' total effects on the gasification. Compared impregnated with acid washed samples, neither nickel nor iron nitrate increase significantly the reactivity. Only for Anglesea brown coal a positive effect was observed. The iron impregnation delivered only a slightly improvement, but $Ni(NO_3)_2$, especially 0.2 Ni improved the maximum reactivity by 20 %. Moreover, the nickel impregnation decreased the burnout temperature by 40 ºC. For German and Loy Yang brown coal, the impregnation had even an impact effect on the reactivity. Either the reactivity decreases or the temperature of the maximum reactivity increases. For the other coal samples, the impregnation has hardly an effect, but one can definitively say that the impregnation with iron and nickel nitrate solution had no positive catalytic effect on the CO_2 gasification for most of the investigated brown coals.

In the following table the maximum reactivity and the associated temperature of the maximum of the different coals after different treatments are shown.

Table 4: Maximum reactivity $\cdot 10^4$ and associated temperature in ºC at 20 % CO_2 gasification after different treatment

Treatment	German lignite		Anglesea brown coal		Loy Yang brown coal		Maddingley brown coal		Yallourn brown coal	
	reactivity	Temp	reactivity	Temp	reactivity	Temp	reactivity	Temp	reactivity	Temp
Raw coal	4.34	930	3.86	980	4.07	1020	3.63	865	4.88	875
1 M HNO_3 washing	3.98	1035	2.86	1060	4.21	1135	3.20	1150	3.18	1045
0.1 M $Fe(NO_3)_3$	3.58	1040	3.29	1080	3.22	1150	2.79	1110	3.25	1035
0.2 M $Fe(NO_3)_3$	3.14	1055	3.45	1074	3.03	1145	2.80	1115	2.87	1035
0.1 M $Ni(NO_3)_2$	3.72	1055	3.32	1020	3.14	1145	3.28	1154	3.00	1030
0.2 M $Ni(NO_3)_2$	3.56	1100	3.42	1000	2.89	1155	2.99	1150	3.15	1035

Table 4 illustrates that the reactivity after acid washing decreases for German, Anglesea and Maddingley brown coals for about 10%, because nearly all catalytic active minerals were eliminated. For Yallourn brown coal the maximum reactivity decreases for more than 35 %. This exclusion is due to the sharp peak of the raw coal reactivity. The reason for this drastically rise is the high iron content of the raw coal.

Not only Yallourn raw coal, but also all iron impregnated samples show a sharp peak in their reactivity curve. That peak is caused by the reaction of iron with CO_2. The reaction enthalpy for this reaction is around 40 kJ/mol lower than the reaction of carbon with CO_2. As a consequence, the iron CO_2 reaction takes places at lower temperatures. Thus a sharp peak before the peak of the real maximum can be expected.

The decrease in reactivity after impregnation might be due to structural changes in the coal. Impregnation may destroy the coal structure and clogging the coal pores. As most reactions take place in the pores on the inner surface of the coal particles. If pores are plugged the gasifying agents cannot reach the inner surface. Hence the coal sample cannot react exhaustively, which results in a lower reactivity. But these speculations need to be investigated in the future.

3.4.2 Gasification with 20 % CO_2 and 15 % steam

The estimated curve shapes should be expected similarly to those from the CO_2 gasification of the previous chapter. One expects also a two-peak distribution of reactivity but the reactivity should generally be higher. As steam gasification requires a lower activation energy compared with CO_2 gasification. As a consequence, the maximum reactivity should be shifted to lower temperatures and should generally be higher than those in CO_2 gasification. Furthermore, a sharp peak in the reactivity of the iron impregnated samples as appeared in the CO_2 gasification, cannot be observed. The reaction of iron with CO_2 has a reaction enthalpy of roughly 120 kJ/mol and the reaction of carbon with water of 130 kJ/mol. Those values lie very close together. As a result, those peaks will overlap and a sharp single peak should not be expected.

The starting of the steam injection has an effect on the microbalance. That is why the reactivity curve shows small, sharp peaks in the range from 180 ºC, where the injection started, until approximately 250 ºC. This unstable range depends on how fast a constant steam flow was set and how often one had to adjust the flow.

3.4.2.1 Reactivity of German lignite

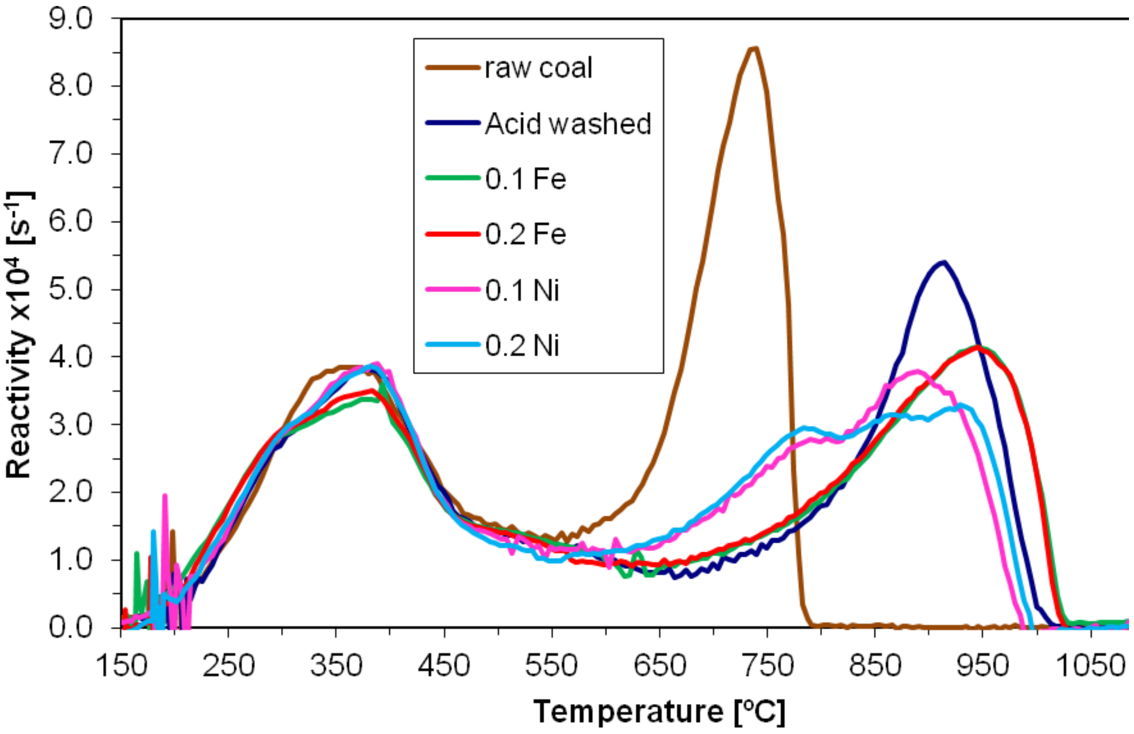


Figure 27: Reactivity of German lignite on steam gasification after different pre-treatment

Figure 27 shows the expected course. The first peak at around 350 ºC refers to the devolatilization of volatiles, as explained in the previous chapter. Just as the reactivity towards CO_2 gasification, the first peak is hardly influenced by the pre-treatment. The 1 molar HNO_3 washing was very successful for the German lignite thus most of the inorganic minerals were removed. This can be proved by the much lower maximum reactivity and the shift of the peak by 80 ºC to the higher temperature for the acid washed coal. Moreover, the burnout temperature increases for more than 200 ºC.

The curves of the 0.1 M and the 0.2 M iron impregnation run nearly similarly. Hence the Fe^{3+} concentration plays no role. Moreover, the reactivity, associated temperature and burnout temperature even increased, thus $Fe(NO_3)_3$ impregnation has no catalytic effect.

After nickel impregnation, the reactivity starts climbing up at a lower temperature, at approximately 600 ºC, compared to the acid washed coal where the reactivity curve rises at 670 ºC. Moreover, the maximum reactivity peak of 0.1 Ni is shifted about 50 ºC towards lower temperature. In summary, Ni^{2+} shows a little catalytic effect, proved by the temperature shift, but the burnout temperature stays almost the same.

3.4.2.2 Reactivity of Anglesea brown coal

The following figure shows the results of the gasification of Anglesea brown coal.

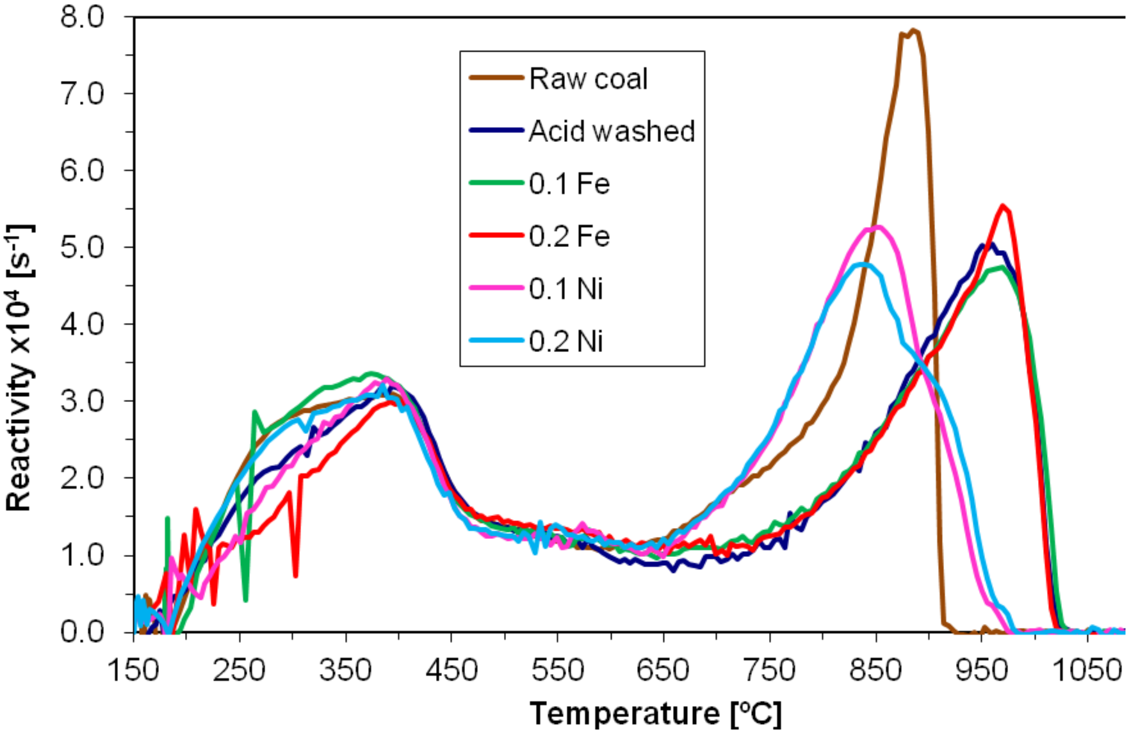


Figure 28: Reactivity of Anglesea brown coal on gasification with CO_2 and steam after different pre-treatment

The 20 % CO_2 with 15 % steam gasification of Anglesea brown coal shows a similar result like the German lignite. The main differences appear in the Nickel impregnated curves. For Anglesea brown coal $Ni(NO_3)_2$ has a positive catalytic effect. The maximum reactivity increased slightly compared to the acid washed coal. The temperature of the maximum reactivity is shifted to lower temperature for even more than 100 ºC. Additionally, the burnout temperature decreases for approximately 40 ºC. To increase the overall efficiency, it is required to reduce the heating cost. If the coal is impregnated with $Ni(NO_3)_2$ it can reduce the gasification temperature, which means less heat input required.

Fe^{3+} shows in contrast no definite effect. The reactivity is nearly the same after impregnation and a temperature shift cannot be spotted. The increase in reactivity after the 0.2 M Fe impregnation is so marginal, which can be neglected.

No curve contains a plateau or a shoulder in their reactivity like observed in Figure . The reason for that phenomenon is the overlapping of the iron carbon dioxide with the carbon steam reaction. As a consequence, those peaks interleave and one cannot recognize two peaks and a shoulder, respectively.

3.4.2.3 Reactivity of Loy Yang brown coal

The acid washing has only a slight effect on the reactivity of Loy Yang brown coal. Loy Yang brown coal contains mainly catalytic inactive mineral species like silicon and aluminium. Thus, the maximum reactivity stays nearly constant and the associated temperature and the burnout temperature increase for only 35 ºC.

The impregnation of $Fe(NO_3)_3$ delivers no effect. It can also be seen that there is no difference between 0.1 and 0.2 Fe^{3+}, which means that the gasification reactions are unaffected. The reactivity after nickel impregnation shows a two-peak distribution in the gasification range. The reactivity starts to rise already at around 600 ºC, so nearly 100 ºC lower than the other curves. Thus it reaches the first maximum much earlier than the acid washed sample. Even the second maximum and the burnout temperature are 40 ºC lower than for the acid washed. Especially due to the early rise of the reactivity and the lower burnout temperature, $Ni(NO_3)_2$ has a positive catalytic effect.

The following plot shows the reactivity of Loy Yang lignite on CO_2 and steam gasification against temperature.

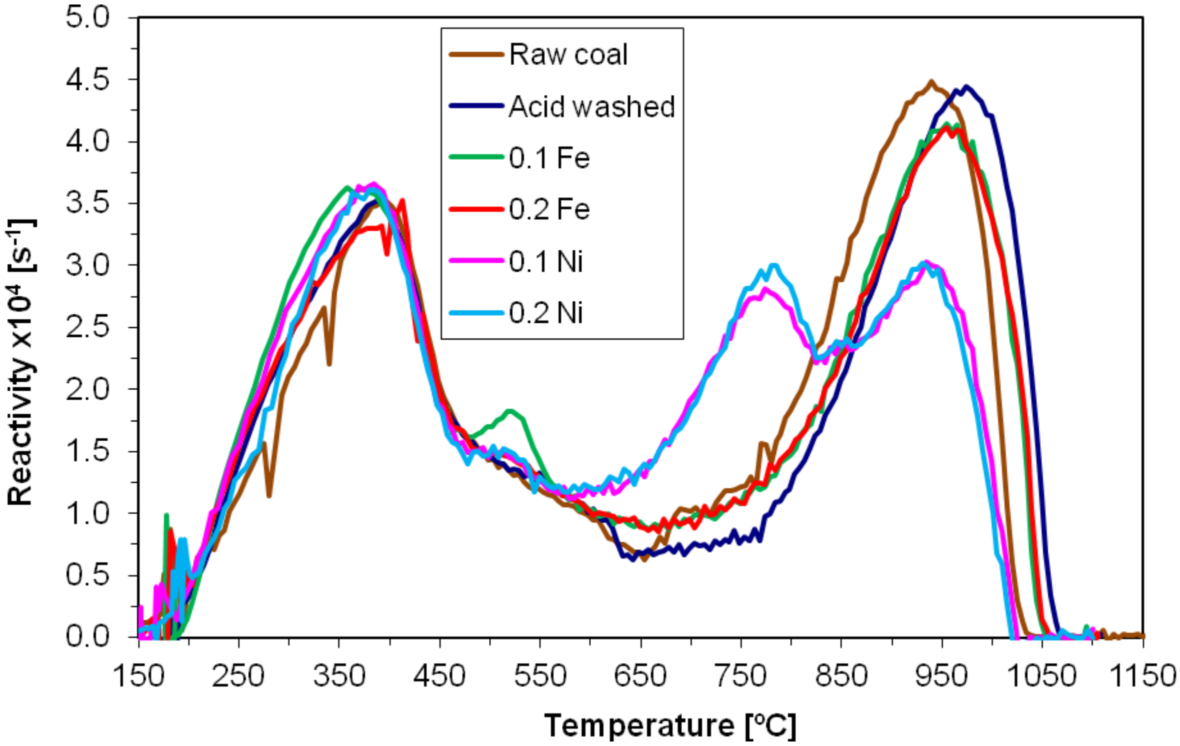


Figure 29: Reactivity of Loy Yang brown coal on gasification with CO_2 and steam after different pre-treatment

3.4.2.4 Reactivity of Maddingley brown coal

Figure 30 shows that Maddingley and Anglesea brown coal behave nearly similarly in a CO_2 with steam gasification environment. On the one hand iron impregnation shows no effect and on the other hand nickel has a great impact on the reactivity in the gasification range. The reactivity curves of the iron impregnated samples show approximately the same progress like the acid washed coal. Moreover, the one molar HNO_3 washing decreases drastically the reactivity and increases the burnout temperature for more than 160 ºC. After $Ni(NO_3)_2$ impregnation the maximum reactivity increases for 7 % and the associated temperature decreases for about 120 ºC. As for Anglesea brown coal, 0.1 M $Ni(NO_3)_2$ delivers the best results.

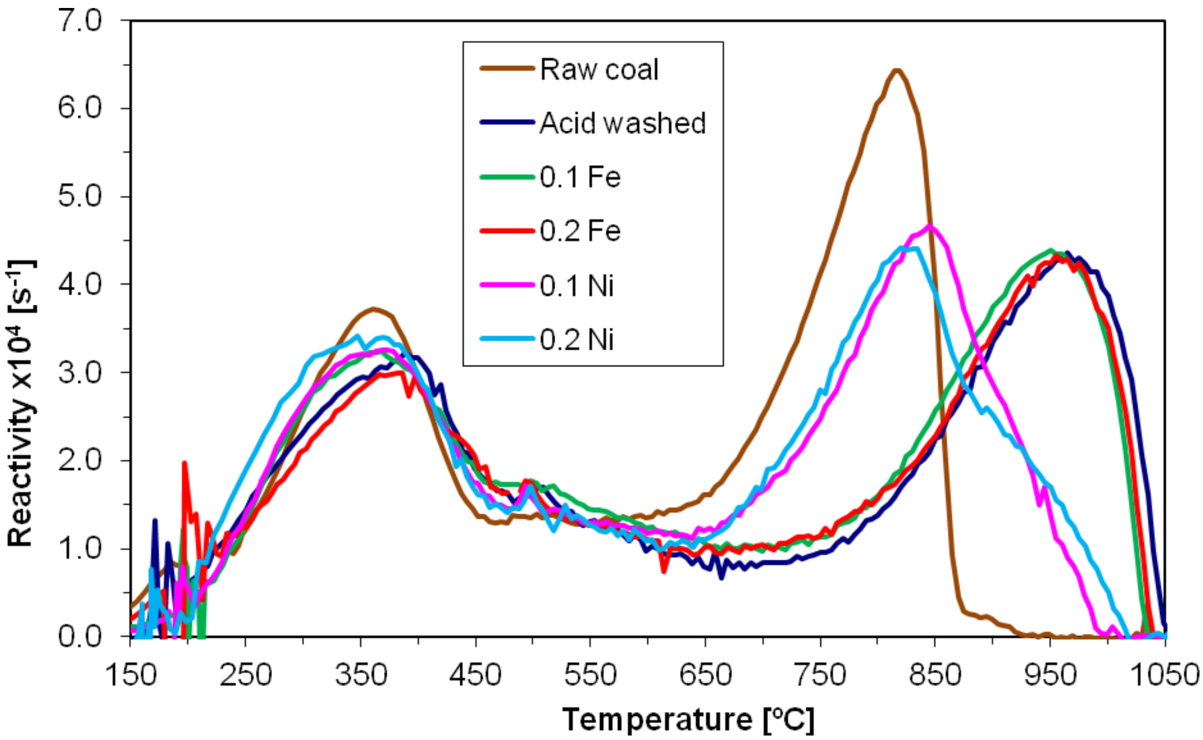


Figure 30: Reactivity of Maddingley brown coal on gasification with CO_2 and steam after different pre-treatment

3.4.2.5 Reactivity of Yallourn brown coal

Yallourn brown coal appears like Anglesea and Maddingley brown coal. Acid washing reduces significantly the maximum reactivity and increases the associated temperature and the burnout temperature. Only nickel impregnation affects the reactivity, iron has no effect on the gasification with CO_2 and steam. Different to the other brow coal, $Ni(NO_3)_2$ impregnation, especially 0.1 Ni increases the maximum reactivity for about 25 %. 0.2 Ni delivers not as good results like 0.1 Ni. Moreover, for the other coals the reactivity curve increased much earlier for the nickel impregnated samples, but this cannot be observed that obviously.

The raw coal does not show the sharp peak like the curves from the CO_2 gasification. The reason is due to the similar reaction enthalpy of the reaction of iron with CO_2 and carbon with water. Therefore, the reactivity peaks are overlapping and thus it does not receive a single sharp peak. The following plot shows the reactivity of Yallourn brown coal towards 20 % CO_2 and 15 % steam gasification against temperature.

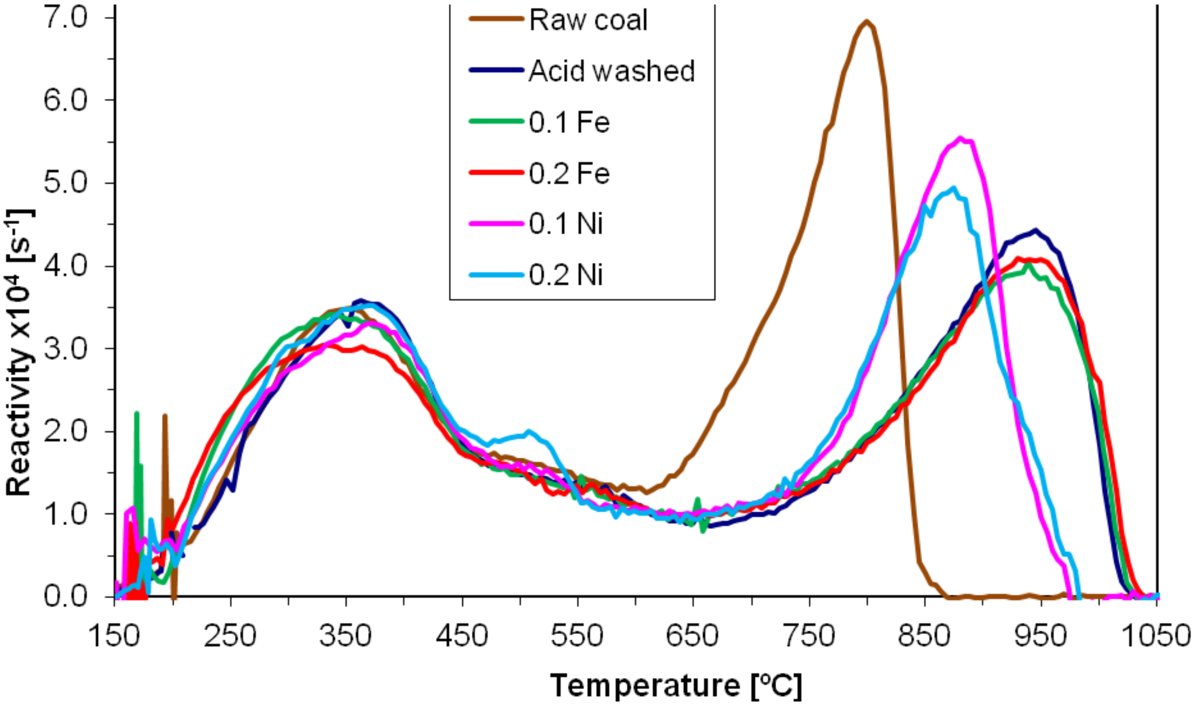


Figure 31: Reactivity of Yallourn brown coal on gasification with CO_2 and steam after different pre-treatment

3.4.2.6 Summary of 20 % CO_2 and 15 % steam gasification

The gasification with CO_2 and steam generates, like the CO_2 gasification a two-peak distribution of the reactivity. The first peak in the temperature range from around 250 till 450 °C is caused by devolatilization of volatiles. Neither acid washing nor ion impregnation affects the reactivity in that region. Hence devolatilization is unaffected by catalytic effects. The second peak results from the reaction of carbon with CO_2 and with steam. As Figures 27-31 show, this region is strongly affected by the pre-treatment of the coal.

The investigation of brown coals can be divided into two groups: One group, where nickel impregnation causes more than one peak in the gasification range and a second group where only one peak can be identified. The first group consists of German lignite and Loy Yang brown coal. Anglesea, Maddingley and Yallourn brown coals belong to the second group. In the following table the maximum reactivity and the associated temperature in the gasification range of the different coals after different treatments is summarized.

Table 5: Maximum reactivity (x10^4) and associated temperature in ºC for 20% CO_2 and 15 % steam gasification after different treatment

Treatment	German lignite		Anglesea brown coal		Loy Yang brown coal		Maddingley brown coal		Yallourn brown coal	
	reactivity	Temp	reactivity	Temp	reactivity	Temp	reactivity	Temp	reactivity	Temp
Raw coal	8.57	840	7.82	885	4.48	940	6.43	815	6.96	800
1 M HNO_3 washing	5.36	915	5.05	960	4.44	974	4.36	965	4.43	945
0.1 M $Fe(NO_3)_3$	4.14	944	4.74	970	4.14	955	4.39	950	4.04	939
0.2 M $Fe(NO_3)_3$	4.14	945	5.54	970	4.12	955	4.33	955	4.08	940
0.1 M $Ni(NO_3)_2$	3.78	890	5.27	855	3.03	935	4.67	845	5.54	880
0.2 M $Ni(NO_3)_2$	3.30	929	4.79	840	3.02	930	4.42	820	4.95	874

The results in table 5 that the 1 molar HNO_3 washing has a deep impact on the reactivity. Nitric acid is a strong acid, hence it can remove most inherent mineral matter from the coal, which results in a much lower reactivity of all investigated coals except Loy Yang brown coal. The acid washing of Loy Yang coal causes only a little temperature shift of the maximum reactivity. The reason for that behaviour lies in the mineral matter content. As it can be seen from Table 2, Loy Yang brown coal contains mostly silica, which has no catalytic effect, and very less of the catalytic active species. Hence, acid washing does not show the same effects like for the other samples.

Furthermore, $Fe(NO_3)_3$ has no positive catalytic effect on the investigated brown coals. Moreover, 0.1 M Ni impregnation delivers the best results for all Victorian brown coals. It is assumed that 0.2 M Ni^{2+} impregnation is over the saturation. For the coals in the first group, nickel has hardly a positive effect on the gasification reactivity. $Ni(NO_3)_2$ increases the reactivity for brown coals in the second group and decreases the temperature of the maximum reactivity for the coals of both groups. Additionally, it decreases the burnout temperature of the coals from the second group. Furthermore, the reactivity after nickel impregnation starts to increase at around 100 ºC earlier than the acid washed samples. A temperature shift corresponding to the maximum reactivity and a decrease of the burnout temperature make it possible to reduce the required heat input. As a result, not only the maximum reactivity but also the associated temperature is important to the boiler designing in the powder generators.

A sharp peak cannot be observed in the iron impregnated curves like those observed on CO_2 gasification, due to the overlapping of the iron reaction with the reaction of carbon with steam. Both reaction types have nearly the same reaction enthalpy. Hence, the reactions take place at almost the same temperature.

3.4.3 Effect of different catalyst loading methods

The mechanical mixing with 1 wt % $Ni(NO_3)_2$ delivers for all coals a higher maximum reactivity, except for Anglesea brown coal. For Loy Yang and Maddingley brown coal it lowered additionally the associated peak temperature. The burnout temperature decreased or stayed equal for all investigated brown coals. The reactivity increase varies from more than 30 % for Yallourn brown coal to a decrease of around 6 % for Anglesea brown coal. The highest decrease of the peak temperature delivers from Maddingley brown coal with 45 ºC. The impregnation with 0.1 M $Ni(NO_3)_2$ solution decreased the maximum reactivity, but also decreased the associated temperature, except for Yallourn brown coal.

The following table displays the maximum reactivity of the different brown coals after the different impregnation methods.

Table 6: Maximum reactivity (x10^4) and associated temperature in ºC for 20 % CO_2 and 15% steam gasification after different catalyst loading

Treatment	Anglesea brown coal		Loy Yang brown coal		Maddingley brown coal		Yallourn brown coal	
	reactivity	Temp	reactivity	Temp	reactivity	Temp	reactivity	Temp
Raw coal	7.82	885	4.48	940	6.43	815	6.96	800
0.1 M $Ni(NO_3)_2$	6.64	840	3.05	935	6.17	760	6.14	819
1 % $Ni(NO_3)_2$	7.36	890	5.50	925	6.55	769	8.12	820

The following figure shows the maximum reactivity of Maddingley brown coal with different mass percentage of $Ni(NO_3)_2$. 0 % Nickel means the raw coal. All curves except the raw coal curve reached its maximum at the same temperature of 780 ºC.

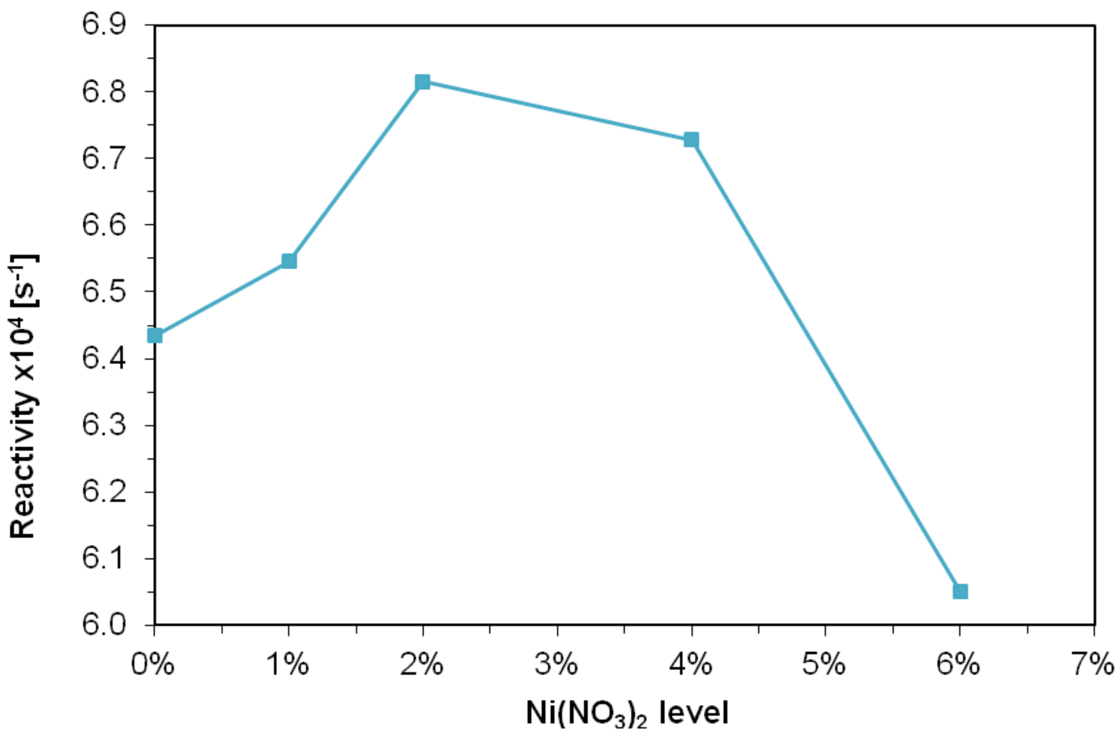


Figure 32: Reactivity of Maddingley brown coal with different Ni(NO$_3$)$_2$ concentration

As it can be seen that the maximum reactivity increases for 1 and 2 wt % reaches its maximum and then decreases after 2 wt % Ni(NO$_3$)$_2$. The maximum reactivity of Maddingley brown coal can be improved by maximal 6 % with mechanical mixing with Ni(NO$_3$)$_2$. The decrease denotes that the mixture is oversaturated after 2 wt % Ni(NO$_3$)$_2$. This means that a certain amount of nickel nitrate has a positive effect, but once the load amount is over the saturated limit, the extra loading has a dramatic impact on the reactivity. Another reason might be the lower carbon content. The higher the nickel loading, the lower is the carbon content, e.g. a loading with 6 wt % Ni(NO$_3$)$_2$ means 3 mg less coal, which results in a lower reactivity.

For mechanical mixing less catalyst is needed to achieve the same reactivity as impregnation with Ni(NO$_3$)$_2$ solution. Moreover, the mechanical mixing is much easier to handle, therefore, this method could find its application in industrial gasification plants.

3.4.4 Comparison of gasification reactivity between German and Victorian brown coals

German lignite has nearly the same carbon hydrogen, nitrogen and sulphur content compared to the Victorian brown coals. Only Maddingley brown coal has lower carbon content and Anglesea brown coal much higher sulphur content. In general Victorian brown coals have much higher moisture content. Moreover, German lignite has a brown colour, whereas Victorian brown coals are almost black.

The ash content of German lignite is higher compared to Anglesea, Loy Yang and Yallourn brown coal. Maddingley brown coal breaks ranks with a higher ash content more than three times compared to the other Victorian brown coals. German lignite has by far the highest calcium content, which is also responsible for the high reactivity. Calcium has a strong catalytic effect on gasification whereas silicon and aluminium have nearly no effect. [4, 24]

Towards CO_2 gasification German lignite would have the highest reactivity if one neglects the sharp peak of Yallourn brown coal due to the reaction of iron with CO_2. The maximum reactivity would then be around 6 % higher for Loy Yang brown coal and more than 10 % higher for all other coals. But Loy Yang brown coal reaches its maximum 90 ºC later. The impregnation with either iron or nickel nitrate delivers like for the other coals no positive effect.

The gasification reactivity of German lignite with 20 % CO_2 and 15 % steam as gasifying agents has by far the highest value and the lowest associated temperature. Only Maddingley reaches its maximum earlier, because of its high mineral content.

To put it in a nutshell, one can say that the tested German lignite is more reactive than the Victorian brown coals.

3.5. Catalytic effect of sodium in coal on combustion reactivity

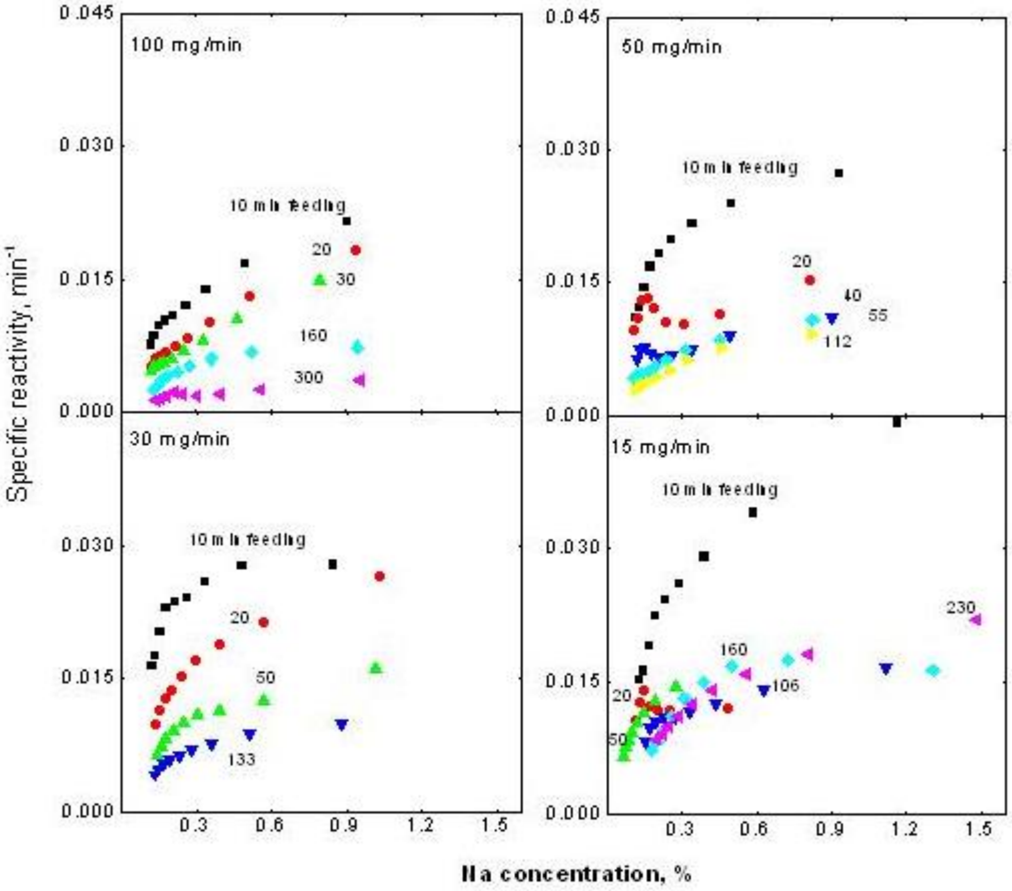


Figure 33 Specific reactivity in air at 400 °C as a function of Na concentration.
Chars were prepared from gasification in steam with continuous volatile-char interactions at different feeding rates at 800 °C.

In this section, we briefly assess and discuss the effect of sodium concentration in coal on its combustion reactivity measured in the TGA using air.

The specific reactivity of chars was plotted against Na concentration as it is exhibited in Figure 33. Generally, for a given Na concentration, the char reactivity varied considerably. In other words, the specific reactivity of chars was not proportional to the content of Na. The reactivities of some samples did not change too much while the Na concentration increased from ~0.15 to 1.2 %, especially for the char prepared at a feeding rate of 100 mg/min with 300 min feeding. For the feeding rates from 100 to

30 mg/min, the reactivity largely reduced with increasing volatile-char interactions time (feeding time) for any given Na concentration. However, the effect of the interactions time was getting much less significant when the feeding rate was further lowered to 15 mg/min. The datum points crossed each other from one sample to another except the sample from 10 min feeding.

The phenomena that char reactivity was not closely related with Na concentration imply that the char structure or carbon skeleton was actually playing a dominant role for the reactivity in the case. The char structure could become more inert through interacting with H radicals derived from volatiles. The effect of H radicals turned to be unimportant when the feeding rate was given as low as 15 mg/min.

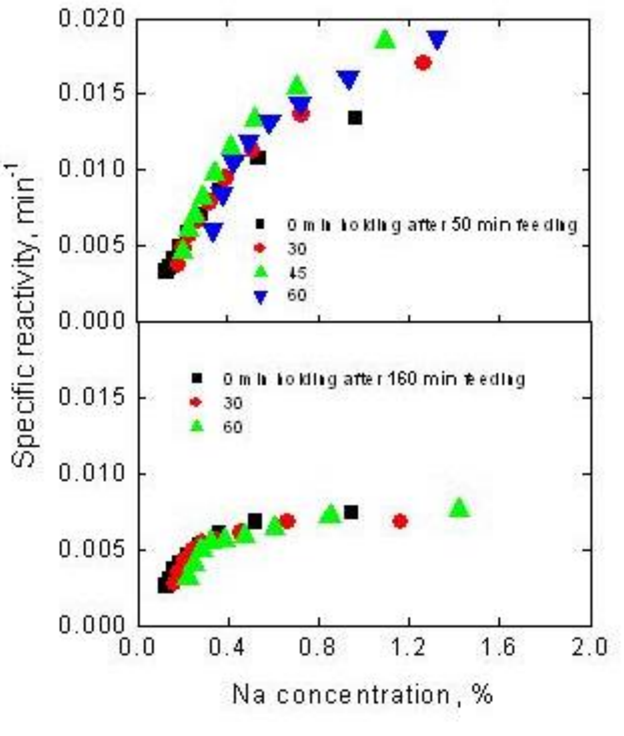


Fig. 34. Specific reactivity in air at 400 °C as a function of Na concentration
Chars were prepared from gasification in steam for different holding time (without volatile-char interactions) after 50 and 160 min feeding respectively at 800 °C.

Figure 34 shows changes of specific reactivity with Na concentration for the chars with different holding time in steam. It can be clearly seen that the specific reactivity increased at different rates regardless of holding time in steam in two circumstances. This indicates that the reactivity of chars with different holding time (in the absence of volatiles) was determined by concentration of Na if the initial feeding time was same.

3.6 Gas clean-up and volatile reforming

Figure 35 shows the NO concentrations in gas production after passing through fixed-bed with filling two Ni-char supported catalysts prepared in 3000 ppm O_2 and argon, respectively. For Ni-char supported prepared in 3000 ppm O_2, NO concentration tends to be zero in 20 minutes, while for Ni-char prepared in argon, NO concentration kept constant level of 10 ppm. All char supported catalysts including Fe-char, Ni-char with 10% and 1% have 100% removal abilities of H_2S.

Experimental results showed that Fe-char and Ni-char have high ability to reform the tar, especially for catalysts prepared in a certain condition. For example, the Ni-char catalyst with 1% Ni-content prepared in 3000 ppm O_2, exhibited very high ability to destroy tar in the gas production. For this catalyst, the outlet section at room was not observed any yellowish matter (tar) as shown in Figure 36.

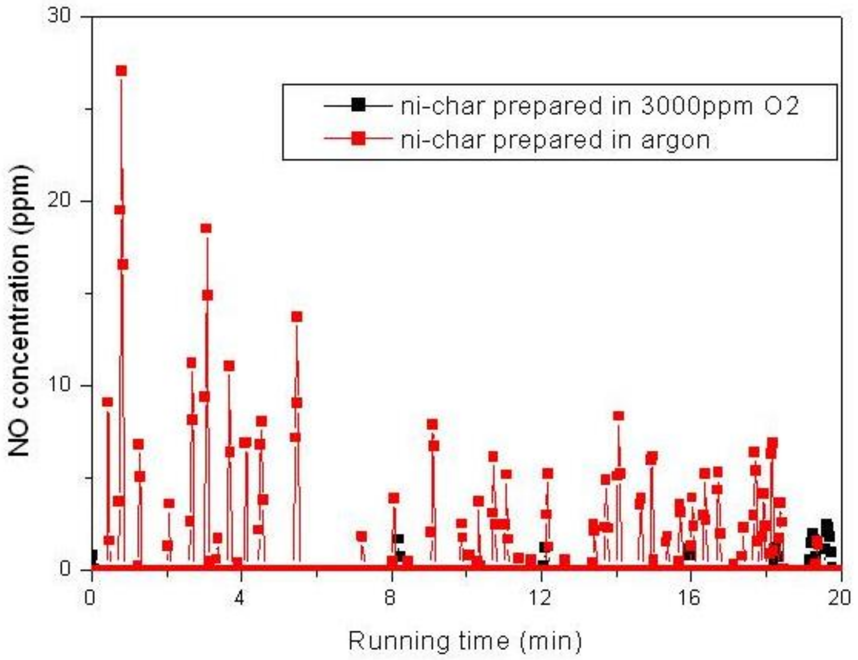


Figure 35 NO concentration in gas production after passing through fixed-bed with two Ni-char supported catalysts prepared in 3000 ppm O_2 and argon, respectively.

Figure 36 Tar at the outlet of the reactor after passing through a fixed-bed with and without catalyst.

Left: After gasification in mixture of 3000 ppm O_2 *and 15% steam balanced with Ar, volatile went through Ni-char (1.8g) prepared at 3000 ppm* O_2

Middle: After gasification in mixture of 3000 ppm O_2 *and 15% steam balanced with Ar, volatile went through Ni-char (1.8g) prepared at argon.*

Right: After gasification in mixture of 3000 ppm O_2 *and 15% steam balanced with Ar, volatile no further reforming.*

Similar observations were made while conducting experiments with other catalysts as well including flyash from Yallourn power station.

While all catalysts were found to be equally effective in cracking tar, our experience with running large fluidized bed gasifier suggest that tar can be minimised or avoided by introducing oxygen or steam in the freeboard of a fluidized bed gasifier.

3.7 Water gas shift reaction

The water-gas shift (WGS) reaction is applied for processing of syngases to change the CO:H_2 ratio for chemicals production. Water-gas shift reaction involves the reaction of CO with steam to produce CO_2 and H_2 :

$CO + H_2O == CO_2 + H_2$

The reaction results in higher yield at lower temperature, but with one downside that the rate of reaction decreases substantially at lower temperature. Catalysts play an important role in achieving reasonably high reaction rates for the water-gas shift reactions at sufficiently low temperatures. Catalysts, need to be economically attractive, being fine particles should be non-toxic. Iron has shown the potential to remove tarry materials [18]. There have been successful attempts to use char-based catalysts for water-gas shift reaction [18]. Another, potentially financially attractive, alternative is to directly use iron oxide. In this work, we investigate effectiveness of char-based iron catalyst and pure iron oxide, as the catalyst, in water-gas shift reactions.

We have used a number of catalysts and compared the catalytic effect of them. We have used fly ash, char-supported iron, char-supported nickel, alumina supported iron, alumina supported nickel. We have preformed the experiments at few different temperatures. The gas injected to the system was a simulated gas consisted of CO, Argon and steam. Table 7 shows the experimental conditions. All particles used in the experiments are of 28-38 micron size. Glass beads were used in the reactor to ensure dispersion of the catalysts.

Table 7. Water gas shift reaction experimental conditions

Exp (No.)	Catalyst	Glass bead height	Flow rate	steam flowrate (mg/min)	temp
1	Yallourn fly ash	0	1	0.1	300
2	Yallourn fly ash	0	1	0.1	300
3	LY Fe	0	1	0.1	300
4	LY Fe	0	1	0.1	300
5	Yallourn fly ash	0	1	0.1	300
6	Yallourn fly ash	0	1	0.1	350
7	Yallourn fly ash	0	1	0.1	400
8	LY Char- Fe	0	1	0.1	300
9	LY Char- Fe	0	1	0.1	350
10	LY Char- Fe	0	1	0.1	400
11	none	1 cm	1	0.1	350
12	none	3 cm	1	0.1	350
13	none	6 cm	1	0.1	350
14	none	12 cm	1	0.1	350
15	none	12 cm	2	0.1	350
16	none	12 cm	3	0.1	350
17	none	24 cm	3	0.1	300
18	none	24 cm	1	0.1	350
19	none	24 cm	2	0.1	350
20	none	24 cm	3	0.1	350
21	none	24 cm	1	0.1	200
22	none	24 cm	1	0.1	250
23	none	24 cm	1	0.1	300
24	none	24 cm	1	0.1	400
25	none	24 cm	1	0.3	350
26	none	24 cm	1	0.4	350
27	none	24 cm	1	0.5	350
28	none	24 cm	1	0.6	350
29	none	24 cm	2	0.15	350
30	none	24 cm	3	0.15	350
31	none	24 cm	2	0.15	250
32	none	24 cm	2	0.2	250
33	none	24 cm	2	0.25	250
34	none	24 cm	2	0.3	250
35	none	max	2	0.15	250
36	none	max	2	0.2	250
37	none	max	2	0.25	250
38	none	max	2	0.3	250
39	none	max	2	0.1	250
40	none	max	2	0.1	300
41	none	max	2	0.1	350
42	iron oxide	6 cm	1	0.1	300
43	iron oxide	6cm	2	0.1	300

44	LY Char- Fe	6 cm	1	0.1	300
45	yall fly ash	6 cm	1	0.1	300
46	LY Ni	6 cm	1	0.1	300
47	Ni Oxide	6 cm	1	0.1	250
48	Ni Oxide	6 cm	1	0.1	300
49	LY Ni	6 cm	1	0.1	300
50	LY Fe	6 cm	1	0.1	300
51	Ni Oxide	6 cm	1	0.1	300
52	iron oxide	6 cm	1	0.1	250
53	iron oxide	6 cm	1	0.1	300
54	LY Ni	6cm	1	0.1	250
55	LY Ni	6 cm	1	0.1	350
56	LY Fe	6 cm	1	0.1	350
57	LY Fe	6 cm	1	0.1	250
58	iron oxide	6 cm	1	0.1	350
59	Ni Oxide	6 cm	1	0.1	350
60	Fe Alumina	6 cm	1	0.1	250
61	Fe Alumina	6 cm	1	0.1	300
62	Fe Alumina	6 cm	1	0.1	350
63	Ni Alumina	6 cm	1	0.1	250
64	Ni Alumina	6cm	1	0.1	300
65	Ni Alumina	6 cm	1	0.1	350

To be able to compare the performance of different types of catalysts, the results are presented as percentage of CO_2 produced per gram of catalyst. Figures 37-39 show the CO_2 produced per gram of catalyst for different types of catalyst and at different reaction temperatures.

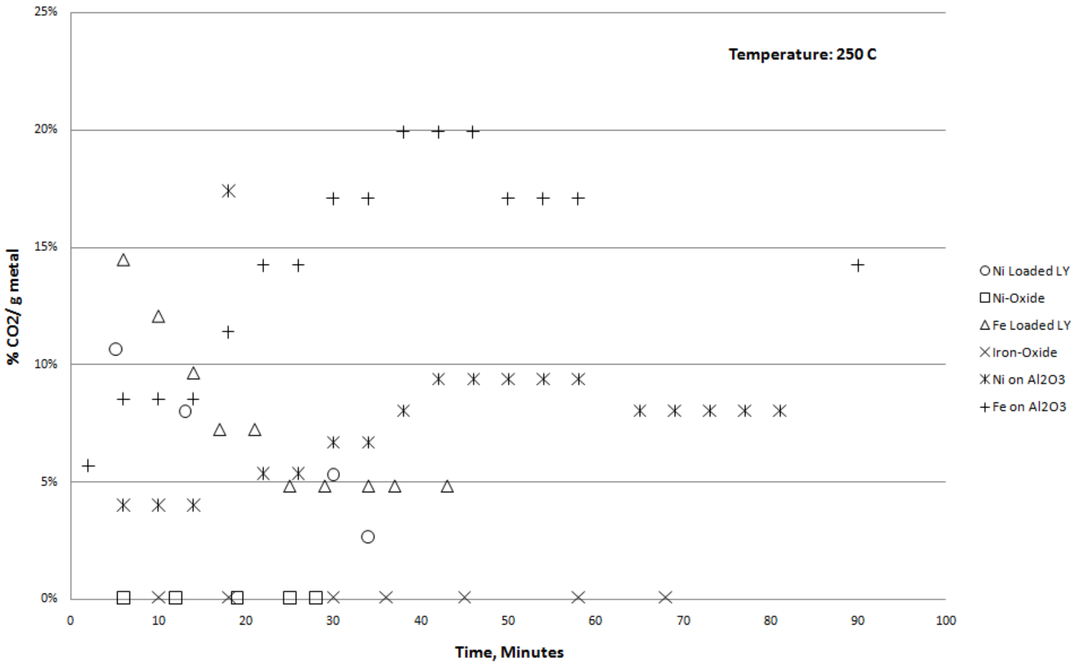


Figure 37 CO_2 production per gram of catalyst, at 250 ºC for different types of catalysts

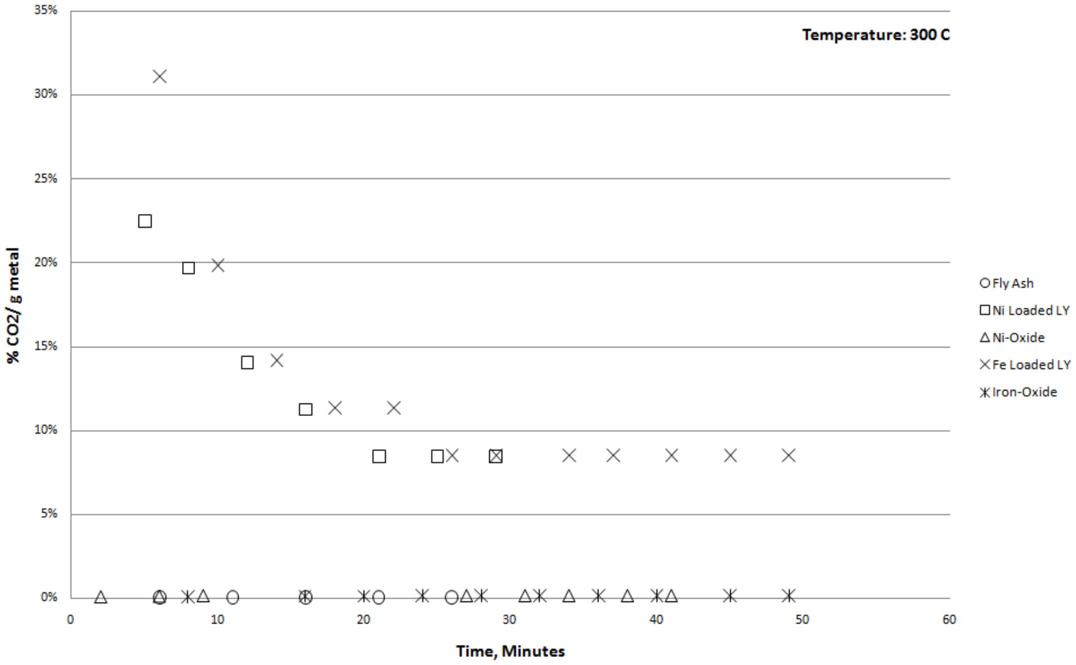


Figure 38 CO_2 production per gram of catalyst, at 300 ºC for different types of catalysts

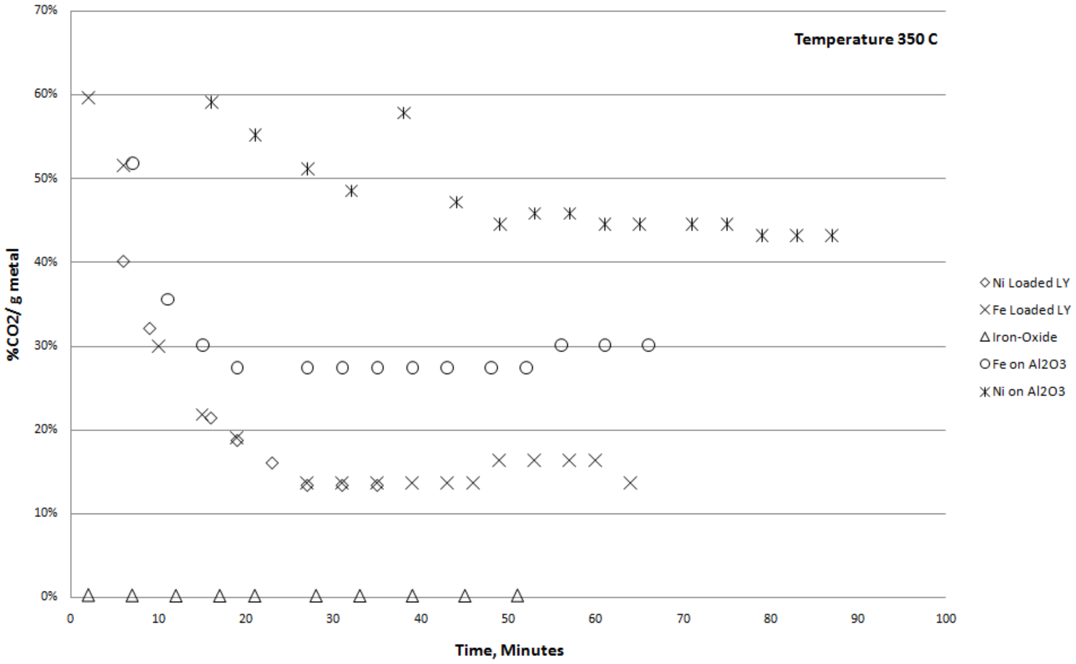


Figure 39 CO_2 production per gram of catalyst, at 350 ºC for different types of catalysts

The results show that fly ash does not show much of catalytic effect. One reason is presumably due to the high crystallinity of the flyash; however, there is a need for further investigation on this matter. It is worth mentioning that we only used Yallourn fly ash, since the iron content in Yallourn coal is shown to be high. Other types of fly ash may have better catalytic performance. Results also suggest that pure Iron Oxide and Nickel Oxide do not seem to have great catalytic effect. It can be due to their crystalline structure, as opposed to the porous structure of char and alumina (as support).

The char supported catalysts and the alumina supported catalysts seem to be more effective in water gas shift reactions. The char supported catalysts, however, tend to disintegrate and deactivate, rather quickly. The activity of the catalysts are in the order of Ni/Alumina > Fe/Alumina > Ni/Char >Fe/Char.

In our system the residence time is rather small. It will be beneficial to carry out the experiments in reactors allowing longer residence time.

4. Concluding comments and recommendations for future work

This report presents results of assessing the effects of a number of catalysts for volatile cracking, gas cleaning and water gas shift reaction and carbon conversion. These catalysts include power station flyash, and Nickel Oxide and Iron Oxide supported on Char, Al_2O_3 and SiO_2.

In addition to the above, the work also included a comparison of gasification reactivity of four Victorian brown coals and a Rhenish lignite obtained from RWE of Germany. This was carried out in thermo-gravimetric analyser under CO_2 and steam gasification atmospheres.

All catalysts were found to be effective in volatile cracking, *ie*. generation of tar-free gas. However, we do not believe that catalysts are required for volatile cracking during gasification.

The major effect of catalysts is found to be on water gas shift reaction. We observed that flyash (collected from Yallourn power station) is not effective at all for water gas shift reaction, presumably because of their higher levels of crystallinity having been exposed to high temperature inside the boiler. On the other hand, Nickel Oxide and Iron Oxide supported on Char, Al_2O_3 and SiO_2 are effective for water gas shift reaction. However, we observed that chars on Char-supported catalysts disintegrate during the water gas shift reaction where steam is present as a reactant. This raises question about the viability of the use of char-supported catalysts continuously in water-gas shift reactors, in particular char from Victorian brown coal which are known to be soft and friable. Considerable effort and trials have to be made to generate char as a support for catalysts, if char from Victorian brown coal is considered for use as a support base for Nickel or iron catalysts.

In addition, Nickel oxide powder is known to be toxic, and therefore its use over a longer-term as a shift catalyst will come under increasing scrutiny. We recommend more focussed work on Fe-based catalysts, supported on either Alumina or Silica base. The work should concentrate on improving and sustaining the activity of such catalysts.

A clear conclusion that emerges from the reactivity measurements and agglomeration modelling is that alternative ways of gasification, such as entrained flow gasification, has to be considered for gasification of Victorian brown coal.

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